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A Study of the Electronic States of 1-Phenylnaphthalene Bridged Phenylnaphthalene and Binaphthyl Derivatives.

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A STUDY OF THE ELECTRONIC STATES OF 1-PHENYLNAPHTHALENE BRIDGED PHENYLNAPHTHALENE AND BINAPHTHYL DERIVATIVES

A Dissertation

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ABSTRACT

The electronic states of 1-phenylnaphthalene, 1,2-benzfluorene, 2,3-benzfluorene, 3,4-benzfluorene 1,2,7,8-dibenzfluorene, 3,4,5,6-dibenzfluorene, benzanthrene and 2,3-benzbiphenylene have been experimentally characterized. The absorption, fluorescence and phosphorescence spectra of all the compounds in rigid glassy solutions at 77°K are shown. The experimental spectra of these composite molecules display absorptive transitions which can be interpreted to correspond to both submolecular and molecular chromophores.

SCFMO calculations of the Pariser, Parr and Pople type including configuration interaction were applied to 1-phenylnaphthalene at ring angles of 90, 55, 45, and 0 degrees and to 2,3-benzbiphenylene. The 2,3-benzbiphenylene calculation indicates that the molecule is fully aromatic. Filled and unfilled molecular orbitals are delocalized over the molecule and all absorptive transitions are characteristic of the whole molecule. Both submolecule and whole molecule transitions are predicted in the case of 1-phenylnaphthalene.

In conjunction with the SCFMO calculation a hydrogen repulsion calculation was carried out. Potential wells were

generated for the ground and the ^1L_a and ^1L_b excited states. The results of the calculations were compared with the experimental observations made on 1-phenylnaphthalene.

With the aid of the zero degree calculation for 1-phenylnaphthalene all the absorptive transitions of the benz- and dibenzfluorene molecules were assigned. These molecules display both whole molecule and submolecule transitions.

CHAPTER I

INTRODUCTION AND THEORETICAL CONSIDERATIONS

Introduction

The electronic states of composite molecules have been a subject of study by workers in this research group for several years. The definition of a composite molecule has varied slightly from worker to worker. The most general definition of composite molecules is the the one that will be employed in this work; composite molecules are defined as molecules which are composed of two or more aromatic subsystems which interact sufficiently to perturb the electronic energy states of two or more of the subsystems. This group of molecules can in the most general terms be divided into two subgroups: the rigid systems of fixed geometry including fluoranthene, the benzfluoranthenes, the biphenylenes, and the fluorenes; and the non-rigid systems of variable geometry including the biphenyls, the phenylnaphthalenes, the binaphthyls, the diaryl alkanes, etc. Although this grouping is geometrically sound and certain molecular spectral characteristics conform to the subdivisions, the grouping does not serve as an aid in interpretations of the electronic states involved.

Generally composite molecules will be characterized by the amount of intramolecular interaction between the electronic states of the aromatic subsystems. The extent of interaction may vary from essentially no interaction to interaction so extensive that the subsystems lose their individual identities and the whole aromatic molecular species must be considered to be the chromophore. Examples of the first kind are numerous. Diaryl alkanes, in general, exhibit absorption spectra which are characteristic of the superposition of the absorption spectra of the submolecular species. Usually through twisting of the alkane chain the submolecules are sufficiently close to each other that intramolecular energy transfer takes place and luminescences from these molecules are characteristic of the submolecule with the lowest energy excited singlet and triplet states. Keller and Dolby[1] have recently studied the molecules 3-(α-naphthyl)-5α-androstan-17β-ol 17β-benzoylbenzoate and 3-(α-naphthyl)-5α-androstan-17β-ol 17-(9-carbazole)acetate. They report that, in sufficiently dilute solutions, emission can be obtained from both the carbazole and naphthalene or benzophenone and naphthalene chromophores. In these cases the submolecular chromophores, in addition to being insulated from each other, are rigidly held at distances far enough from

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[1]Richard A. Keller and Lloyd J. Dolby, J. Am. Chem. Soc., 89, 2768 (1967).

each other so that the emission rates successfully compete with the rate of intramolecular energy transfer. In addition to these sophisticated molecules, simpler molecules such as 9,10-diphenylanthracene exhibit absorption spectra which are little different from those of the submolecular portions.[2,3]

The other extreme of interaction in composite molecules may be represented by molecules such as perylene. In these molecules the submolecules are fused together in such a way that intramolecular interaction is so large that the submolecular identity is lost. The electronic transitions in these molecules are characteristic of the entire molecular chromophore. Between these extremes many composite molecules exist which exhibit varying degrees of submolecular interaction.

Ory[4] and Wharton[5] have studied the electronic transitions of fluoranthene. In addition Wharton has studied the 3,4-benzfluorene, 11,12-benzfluorene and 1,4-dibromo-2,3-benzbiphenylene molecules. The 2-phenylnaphthalene system has been considered by Harris[6] and

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[2]R.N. Jones, J. Am. Chem. Soc., 67, 2127 (1945).

[3]R.A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, John Wiley and Sons, New York, N.Y. (1951).

[4]Horace Ory, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana (1957).

[5]James H. Wharton, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana (1962).

[6]James Harris, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana (1965).

Holloway.[7] In addition Harris has studied several 2-phenylquinolines and Harris and Holloway have studied some of the benzfluorenes. The biphenyl system has been considered by King.[8] Wharton[9] has applied exciton theory to fluoranthene and Holloway[10] has done an antisymmetrized self-consistent field molecular orbital calculation including configuration interaction on the planar 2-phenylnaphthalene molecule. Wharton, in another work currently being prepared for publication, has included hydrogen-hydrogen repulsion and has extended the calculation to other conformations of 2-phenylnaphthalene. All of these composite molecules exhibit a significant interaction between aromatic ring systems and some of their spectra have been interpreted to be characteristic of the submolecular aromatic ring systems.

This research was initiated with the intention of clarifying the anomalies found in the previous studies of these compounds. Holloway found that multiple emissions (more than one molecular fluorescence or phosphorescence) reported for

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[7] H.E. Holloway, Ph.D. Dissertation, Louisiana State University, Baton Rouge, Louisiana (1967).

[8] J.R. King, work to be published.

[9] Wharton, op. cit., pp.5-12.

[10] Holloway, op. cit., p.18.

several compounds were due to trace impurities in these compounds. This discovery required that the spectra of these compounds be re-characterized and that new interpretations be applied to their spectra. In this research most of the remaining anomalies have been studied and the previously unreported electronic states of several other composite molecules have been studied. The molecules studied in this work are shown in Figure 1. The electronic states of these molecules are characterized in this work. The electronic spectra of 2,3-benzbiphenylene and the dibenzfluorenes have not been previously reported. Attempts are made to interpret the spectra of these molecules in the context of the framework of the spectra of composite molecules. Interactions between submolecules vary from minimal in the case of the phenylnaphthalenes to a maximal in the case of 2,3-benzbiphenylene.

B. Characterization of Transitions

There are three commonly used systems for classification of absorptive electronic transitions of aromatic hydrocarbons. The most generally accepted classification is that based on group theory.[11] This system identifies both the ground state and excited state symmetry species. Unfortunately in large molecules

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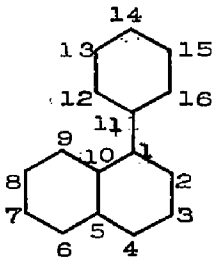
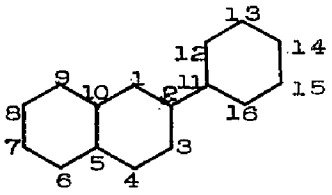
[11] M. Goeppert-Mayer and A.L. Sklar, J. Chem. Phys., 6, 645 (1938).

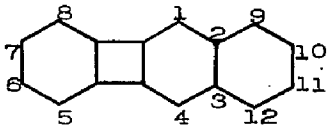
FIGURE 1. Some Hydrocarbon Molecular Structures



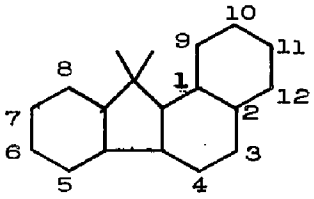
1-Phenylnaphthalene



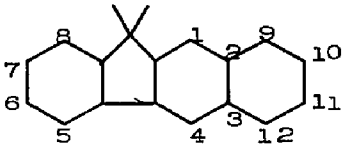
2-Phenylnaphthalene



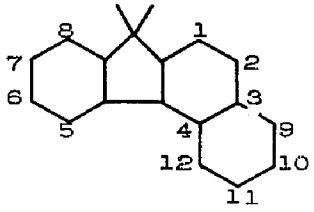
2,3-Benzbiphenylene



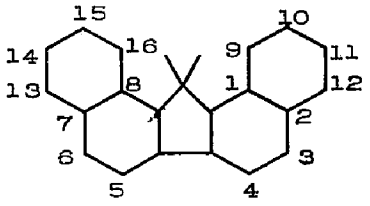
1,2-Benzfluorene



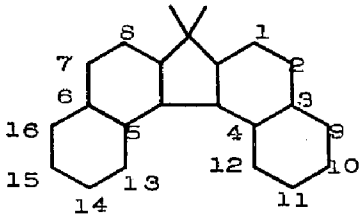
2,3-Benzfluorene



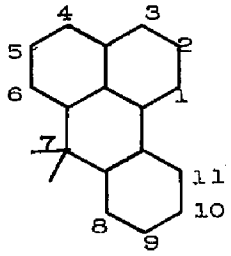
3,4-Benzfluorene



1,2,7,8-Dibenzfluorene



3,4,5,6-Dibenzfluorene



Benzanthrene

that have low symmetry this classification is very hard to apply. In addition, when large molecules exhibit a relatively high symmetry and the symmetry species of the appropriate states is known, so many transitions are exhibited that several transitions invariably possess the same classification. The use of group theoretical notation is employed at times in this work but always in conjunction with other classification systems. Clar[12] has classified the first three transitions in the spectra of many aromatic hydrocarbons as the α, β, and para bands. These transitions are assigned on the basis of observed similarities in intensities and shifts with substitution along given molecular axes. Platt[13] has classified absorption transitions according to a perimeter free electron model. In this classification the α band of Clar corresponds to the $^1A \rightarrow {}^1L_b$ transition, the para band to the $^1A \rightarrow {}^1L_a$ transition and the β band to the $^1A \rightarrow {}^1B_b$ transition. The Platt system designates both the ground and excited states and has the advantage that both absorptive and emissive transitions can be completely characterized. The Clar classification has not been

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[12] E. Clar, Spectrochim. Acta., 4, 116 (1959).

[13] J.R. Platt, J. Chem. Phys., 17, 484 (1949).

widely accepted in recent years and has the additional disadvantage that when an adsorption spectrum has six or seven apparent transitions, classification of them is impossible with the Clar nomenclature. Use of the Platt classification based on the perimeter free electron model loses its theretical justification when it is applied to molecules such as the phenylnaphthalenes. However, many spectroscopists working with large molecules use this system because a better, badly needed, system is unavailable. Although there is no theoretical justification, the Platt nomenclature is used extensively in this work. It is not used in the sense Platt intended,but has been applied much in the spirit of the Clar notation, that is, it is based on similarities in the observed intensities, polarizations, and vibrational progressions with those of benzene, naphthalene, and higher acenes. In addition it has been necessary to further bastardize the Platt system when transitions involving only submolecules are assigned and when transitions must be assigned for which there is no analogue in the Platt system. This has been necessary mainly in conjunction with the theoretical calculations, and attempts are made to limit this practice to that section. When submolecular transitions are assigned and Platt symbolism is used, an additional subscript has been added to the normal notation.

For example a naphthalene submolecule $^1A \rightarrow {}^1L_a$ transition is denoted $^1A \rightarrow {}^1L_{aN}$. Further explanations of the adapted Platt nomenclature are made as it is used. One additional point concerning the Platt system will be made. Since no firm agreement concerning the order that the states be named has ever been reached, as a personal preference, this author chooses to name the lower energy state first and the higher energy state second and to indicate the process involved by use of the conventional arrow.

In conjunction with the Platt and group theoretical notation one further system of notation has been used in the theoretical section. The self-consistent field molecular orbital designation has been used to denote transitions. For example the lowest energy transition in 2,3-benzbiphenylene is theoretically from the highest occupied molecular orbital to the lowest unoccupied molecular orbital. From the self-consistent field calculation this transition is denoted as the ψ_8^9 transition. It is a convenient shorthand notation for a transition taking place between molecular states involving predominantly M.O.8 and M.O.9. From Platt notation it is designated as the $^1A \rightarrow {}^1L_a$ transition and from group theory as a $^1B_1 \rightarrow {}^1A_2$ transition. Each symbolism denotes the same transition for this molecule

but each accentuates slightly different phenomena involved in the transition. Often, more than one notational system will be used, and when only one is employed the one which best makes the point that the author is trying to convey will be used.

C. Molecular Orbital Calculations

Theoretical consideration has been given composite molecules by various authors with varying degrees of limited success. These treatments have been reviewed by Holloway.[14] The most promising theoretical treatment available for large composite molecules and the one employed in this work is the antisymmetrized self-consistent field molecular orbital calculation that includes configuration interaction.

The assumption usually employed in semiempirical self-consistent field (SCF) calculations of the type associated with the names Pariser,[15] Parr and Pople[16,17,18] are so sweeping

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[14] Holloway, op. cit., pp.14-17.

[15] K. Rudenberg, J. Chem. Phys., 34, 1861 (1961).

[16] R.G. Parr, Quantum Theory of Molecular Structure, W.A. Benjamin, Inc., New York, N.Y., 1963.

[17] R. Pariser, J. Chem. Phys., 24, 250 (1956).

[18] J.A. Pople, Trans. Farad. Soc., 49, 1375 (1953).

that, although they can be justified to some extent theoretically,[18] their adoption can ultimately be justified only by the success that their use has achieved in explaining experimental work, in predicting new effects, and in guiding the design of new experiments.[19a] SCF-MO calculations including configuration interaction, CI, have been carried out with amazing success on many polycyclic hydrocarbons. The technique has also had good success in explaining many spectra of substituted aromatics and is reasonably successful when applied to non-alternant hydrocarbons.[19b]

With the exception of biphenyl[20] and 2-phenylnaphthalene,[21] as far as the author was able to discern no serious attempt has been made to apply this technique to composite systems. The SCF-MO with CI scheme was applied to 1-phenylnaphthalene and to 2,3-benzbiphenylene in this work.

The details of approximations introduced by Pople, Pariser and Parr into the closed shell Hartree-Fock method[22] have been described elsewhere.[23] A summary of these approximations

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[19a] J.E. Bloor, Can. J. Chem., 43, 3026 (1965).

[19b] J.E. Bloor, P.N. Daykin, P. Bolton, Can. J. Chem., 42, 121 (1964).

[20] J.E. Bloor, N. Breerley, work to be published.

[21] H.E. Holloway, loc. cit.

[22] J.C. Slater, Quantum Theory of Molecules and Solids, Vol.1, McGraw-Hill Co., New York, N.Y., 1963.

[23] H.C. Longuet-Higgins, Advances in Chemical Physics, 1, Interscience Publishers, Inc., New York, N.Y., p.239, 1958.

will be outlined at this time; the notation of Bloor will be used.

The pi-molecular orbitals MO's are expressed as linear combinations of atomic orbitals, AO's, φ_p.

$$\psi_i = \sum_p^{N\pi} C_{ip}\, \varphi_p \qquad \ldots.1$$

In this calculation the exact form of the AO's is not specified. The one-electron Hartree-Fock problem for closed shell pi-electron systems reduces to the F matrix with the following elements.

$$F_{pq} = H^c_{pq} - \frac{1}{2} P_{pq}\, \gamma_{pq} \qquad p \neq q \qquad \ldots.2$$

H^c_{pq} is the core hamiltonian and γ_{pq} is the two center atomic repulsion integral for adjacent atoms p and q.

$$F_{pp} = H^c_{pp} + \sum_q P_{pq}\, \gamma_{pq} - \frac{1}{2} P_{pp}\, \gamma_{pp} \qquad \ldots.3$$

P_{pq} is an element of the bond order matrix, Eq.4,

$$P_{pq} = 2 \sum_i^{N_{occ}} C_{ip}\, C_{iq} \qquad \ldots.4$$

This sum extends only over the occupied MO's indicated by N_{occ}.

The secular equation (5) is used to determine the eigenvectors C_{ip} and the orbital energies E_i.

$$\sum_{p}^{N\pi} C_{ip} F_{pq} = E_i C_{iq} \qquad \ldots.5$$

The σ-bond framework is included as a part of the core hamiltonian. The eigenvectors C_{ip} in Eq.4 must also satisfy equation (5). Hence it is necessary to use an iterative procedure. This process provides virtual and occupied MO coefficients and energies.

The off diagonal elements of the core matrix are often treated as empirical paramters, β_{pq}. When p and q are adjacent atoms contributing electrons within as aromatic ring, a value for β_{pq} of -2.39 was chosen. Although arbitrary, this value seems to be standard since its proposal for benzene in 1953.[24] The value for β_{pq} between rings was treated as a parameter that was adjusted to obtain a fit with the observed energy levels. The value -2.150, suggested by Streitwieser, was chosen for β_{pq} in the case of 1-phenylnaphthalene.[25] This value provided sufficient agreement with the experimental data for 1-phenyl-naphthalene. The value for β_{pq} for 2,3-benzbiphenylene was varied and a discussion of this procedure will be made later.

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[24] R. Pariser, R.G. Parr, J. Chem. Phys., 21, 446, 767 (1953).

[25] Andrew Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, John Wiley and Sons, Inc., New York, N.Y., 1961, p.103.

The diagonal elements of the core matrix are usually expanded in the manner of equation 6.

$$H^{c}_{pp}(i) = \int \varphi_p(i) \left| T(i) + \sum_{q \neq p} U_q^{n_{q+}}(i) + \sum_s U_s(i) + \sum_p U_p^{n_{p+}}(i) \right| \varphi_p(i) dv \quad \ldots.6$$

$U_q^{n_{q+}}$ represents the potential due to the core of atom q when the n electrons which contribute to the pi-electron system have been removed. U_s represents the potential due to an atom s which does not contribute pi-electrons to the system and T is the kinetic energy operator. Evaluation of the contribution of $(T + U_p^{n_{p+}})$ is made by means of the Goeppert-Mayer-Sklar approximation, Eq.7.[26]

$$\int \varphi_p(i) \left| T(i) + U_p^{n_+}(i) \right| \varphi_p(i)\ dv = E_p = -I_p^{(n-1)_+} \quad \ldots.7$$

$I_p^{(n-1)_+}$ is the valence state ionization potential of atom p and is usually taken from valence state ionization potential tables.

The core terms in the first summation in equation 6 can be written as a potential due to the neutral atom U_q^o followed by a correction term which allows for the repulsion due to the pi-electrons contributed by that atom. Hence when an atom q

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[26] M. Goeppert-Mayer and A.L. Sklar, J. Chem. Phys., 6, 645 (1938).

contributes n pi-electrons to the system,

$$U_q^{n+}(i) = U_q^o(i) - \sum_{j\neq i}^{n} \int \frac{\varphi_q^2(j)}{r_{ij}} dv_{ij} \qquad \ldots.8$$

The diagonal elements of the core matrix can then be expanded as shown in Eq.9.

$$H_{pp}^c = -I_p^{(n-1)} - \sum_{p\neq q} (U_q^o : pp + n_q \gamma_{pq}) - \sum_s U_s : pp \qquad \ldots.9$$

The terms U_q^o:pp and U_s:pp are called penetration integrals for the neutral atoms. The penetration integrals follow the convention that

$$U_s : pp = -\int U_s(i)\ \varphi_p^2(i)\ dv(i) \qquad \ldots.10$$

For the purpose of alternant hydrocarbons the value of H_{pp}^c is the same for all carbon atoms and equals -11.16ev.

The repulsion integrals γ_{pq} are defined by equation 11.

$$\gamma_{pq} = \int \varphi_p(i)\ \varphi_p^*(i)(1/r_{12})\varphi_q(2)\varphi_q^*(2) dv_1 dv_2 \qquad \ldots.11$$

The one center repulsion integrals are calculated by the empirical method proposed by Pariser and Parr.[11] Using data from atomic

spectra one calculates these integrals by the use of Eq.12.

$$\gamma_{pp} = I_p - A_p \qquad \ldots.12$$

Here I_p is the ionization potential of atom p in the appropriate valence state and A_p is the electron affinity for the same valence state. Since as accurate a calculation as possible for the excited states was desired, the two center repulsion integrals were calculated by the procedure proposed by Mataga.[27] In this procedure the repulsion integrals for an internuclear separation r are assumed to be of the form

$$\gamma_{pq}(r) = \frac{14.397ev}{a_{pq} + r_{pq}} \qquad \ldots.13$$

and

$$a_{pq} = \frac{28.794ev}{\gamma_{pp} + \gamma_{qq}} \qquad \ldots.14$$

These values for the repulsion integrals obtained from the SCF-MO calculation are then used for the configuration interaction calculation.

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[27] N. Mataga, and K. Nishimoto, Z. Physik. Chem., (Frankfurt, A.M.) 13, 140 (1957).

The excited states of the molecule Ψ_I can be expressed as linear combinations of individual configurations ψ_i^k as indicated in Eq.15.

$$\Psi_I = \sum_k A_I^{(ik)} \psi_i^k \qquad \ldots.15$$

in which an electron has been excited from a MO ψ_i to another MO ψ_k. Diagonalization of a configuration interaction matrix yields the mixing coefficients $A_I^{(ik)}$ and the excitation energies. The elements of the CI matrix are given by Eq.16.

$$(^1\psi_i^k|H|^1\psi_j^1) = \partial_{ij}\partial_{kl}(E_k - E_i) + 2\langle ik|jl\rangle - \langle ij|kl\rangle \qquad \ldots.16$$

In this equation E_i is the orbital energy of the SCF-MO, ψ_i. The integrals $\langle ik|jl\rangle$ and $\langle ij|kl\rangle$ are molecular repulsion integrals. These repulsion integrals are defined in Eq.17.

$$\langle ik|jl\rangle = \sum_p \sum_q C_{ip}C_{kp}C_{jq}C_{mq}\gamma_{pq} \qquad \ldots.17$$

The oscillator strength f_i of a transition to the I'th excited state of energy E_I is calculated by Eq.18.

$$f_i = 8.753 \times 10^{-2} Q_{0\rightarrow I}^2 E_I \qquad \ldots.18$$

In Eq.18 $Q_{0\rightarrow 1}$ is the transition moment and is given by

$$Q_{0\rightarrow 1} = \int \Psi_o \, e\bar{r} \, \Psi_I dv \qquad \ldots\ldots 19$$

In the calculation on 1-phenylnaphthalene and 2,3-benzbiphenylene, twenty-five configuration interactions were used. Only single electron excitations were considered and these were from the set of highest occupied MO's to the corresponding lowest unoccupied MO's.

CHAPTER II

METHODS AND MATERIALS

A. Solvents

1. Hydrocarbon Solvents

Phillips pure grade solvents isopentane (IP) and 3-methylpentane (3-MP) were purified by stirring them for eight to twelve hours with Mallinckrodt fuming sulfuric acid (20% free SO_3). After the treatment with acid they were washed several times with water, then with a saturated solution of sodium carbonate, and again several times with water. The solvents were dried over anhydrous magnesium sulfate for twenty-four hours and then distilled at a rate of ten to twenty drops per minute. The still consisted of an electrically heated two-liter single necked flask below a thirty inch distillation column packed with glass beads. Solvents were considered pure when they showed no appreciable emission and no appreciable absorption at wavelengths greater than 2100Å. IPMP, a mixture of six parts IP to one part 3-MP by volume was purified as described above and was used for absorption and emission measurements at 77°K.

2. Alcoholic Solvents

Ethyl alcohol: 95% ethanol from U.S. Industrial

Chemical Co. was used without purification.

Ethyl alcohol: Absolute ethanol, Reagent Quality, from U.S. Industrial Chemical Co. was used without further purification.

Methyl alcohol: Fisher, Certified Reagent Grade, methanol was used without further purification.

EPA mixed solvent: This mixture of ethyl ether, isopentane, and ethyl alcohol in a volume ratio of 5:5:2 respectively was made by Hartmann-Leddon Co. Solvent from fresh previously unopened bottles was used to prepare solutions for emission measurements. EPA from bottles which had been opened for a short time was adequate for preparation of solutions for absorption measurements.

Mixed Alcoholic Solvent: This solvent from Hartman-Leddon Co. is a prepared fluorometric grade mixture of methyl, ethyl and isopropyl alcohols. Often, new bottles of this solvent are received in a state of sufficient impurity to render them useless for use in emission measurements.

B. Compounds

1. 1-Phenylnaphthalene

1-Phenylnaphthalene samples from Columbia Organic Chemical Co., Inc. and from K & K Laboratories, Inc. were

vacuum distilled several times; the middle fraction was collected from each distillation. After several distillations the samples were still impure. These samples still produced the low energy delayed fluorescence reported by Harris.[28] In addition NMR spectra of neat samples were run. The NMR spectra showed three bands corresponding to nonaromatic hydrogens. These bands are located at approximately 0.8, 1.7 and 3.1 ppm. The nonaromatic NMR proton signals could not be assigned to any solvent in the laboratory. Although electronic integration was impossible, determination of areas under the curves and application of output level ratios from the instrument indicate that the nonaromatic hydrogen to aromatic hydrogen ratio was approximately 0.037. The commercial samples and the vacuum distilled samples gave approximately the same NMR spectra.

Synthetic 1-phenylnaphthalene was prepared by the following method. Di-1-naphthoylperoxide for the synthesis was prepared by the procedure described by Kharasch and Dannley.[29] Approximately 50 g. of 1-naphthoylchloride dissolved in 70 ml of anhydrous acetone was added to an agitated suspension of 10.6 g. of sodium peroxide in 140 ml. of anhydrous acetone at 0°C and

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[28] James L. Harris, loc. cit.

[29] M.S. Kharasch and R.L. Dannley, J. Org. Chem., 10, 410 (1945).

was stirred overnight. The di-1-naphthoylperoxide separated when the solution was poured into 200 ml. of ice water. The white precipitant was filtered and washed three times with ice water. The crystals were partially dried under vacuum for one hour. The peroxide was reacted with benzene by a procedure analogous to the one described by Hey and Walker for the preparation of 2-phenylnaphthalene.[30] The di-1-naphthoylperoxide was added to one liter of benzene. Approximately 30 ml of water separated from the benzene solution and was removed with a pipette. After the solution had refluxed for twenty-four hours most of the excess benzene was distilled off. The product was refluxed for three hours with 10% aqueous alcoholic sodium hydroxide. The remaining benzene and alcohol was removed by distillation. The organic layer was partitioned into benzene and washed with 10% aqueous potassium hydroxide. Benzene was removed under vacuum and the resulting organic liquid was vacuum distilled in the absence of air and the fractions were stored under nitrogen. Ultraviolet absorption and emission analyses were carried out on the various fractions to determine their purity. Further conclusions about the purity of the synthetic 1-phenylnaphthalene will be drawn in a later section.

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[30] D.H. Hey and W.E. Walker, J. Chem. Soc., 2217 (1948).

2. 2,3-Benzbiphenylene

2,3-Benzbiphenylene was prepared by the synthetic route described by Jensen and Coleman.[31] Wharton[32] carried the synthesis as far as 1,4-dibromo-2,3-benzbiphenylene. The desired compound was prepared from a sample of Wharton's product. N-butyllithium for the synthesis was prepared by the method described in Organic Reactions.[33] A solution of 68.5 g. of butylbromide in 100 ml. of dry ethyl ether was added dropwise to a flask containing 8.6 g. of lithium and 200 ml. of dry ether until reaction started. The reaction mixture was then cooled to -10°C. After the reaction appeared to be complete the temperature was raised to 10°C. and the mixture was stirred for two hours. The mixture was filtered through a tube loosely packed with glass wool and immediately reacted with the dibromobenzbiphenylene. The n-butyl lithium was added to a solution of 10 g. of dibromobenzbiphenylene dissolved in dry ether. After the mixture refluxed for four hours, it was washed with a dilute hydrochloric acid solution and the ether was removed by distillation. The residue was taken up in absolute ethanol and filtered from charcoal several times. The ethanol was removed and the residue was vacuum sublimed. The appropriate

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[31] F.R. Jensen and W.E. Coleman, Tet. Letters, 20, 7 (1959).

[32] James H. Wharton, loc. cit.

[33] Organic Reactions, Vol. VI, p.352.

vacuum sublimation fraction was recrystallized from absolute ethanol. The resulting crystals gave a melting point of 240-242°C. Jensen and Coleman report a value of 242.6-243.2°C. The ultraviolet absorption spectrum was consistent with that predicted from the spectrum of dibromobenzbiphenylene. The NMR absorption spectrum of the sample dissolved in $CDCl_3$ was identical with that reported by Martin et. al.[34]

3. 7H-Benz[de]anthracene (benzanthrene)

Benzanthrene was prepared from 7H-benz[de]anthracene-7-one (benzanthrone) by the general procedure outlined by Brown and White.[35] The reagent for the synthesis was prepared in a dry box. 2.0 g. of $LiAlH_4$ was added to a mixture of 14 g. of $AlCl_3$ in 30 ml. of dry ether. After the vigorous reaction ceased a slurry of the ketone, 6 g. in 300 ml. of dry ether, was added over a 20 minute period. The mixture was refluxed for one hour and then cooled to 0°C. and water was added to destroy the excess reagent. 200 ml. of sulfuric acid (20%) was added and the ether layer and all solids were collected. The ether was removed and the solid was taken up in a minimum amount of benzene. The product was chromatographed on very slightly

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[34] R.H. Martin, J.P. Van Trappen and N. Defay, Tetrahedron, 20, 2373 (1964).

[35] B.R. Brown and A.M.S. White, J. Chem. Soc., 3755 (1957).

activated alumina. The colorless effluent showed strong blue fluorescence. The benzene was evaporated and there remained about 2.5 g. of light orange leaflets which melted sharply at 84.5°C. The ultraviolet absorption spectrum indicated that the product was impure. At this point the product was recrystallized three more times from absolute ethanol. The product was very light yellow leaflets, the absorption spectrum of which showed a lower impurity level. The product from the ethanol recrystallizations was taken up in CCl_4 and chromatographed on very slightly activated alumina. The solvent was evaporated from the effluent and the product was crystallized again from absolute ethanol yielding pure white plates with a melting point of 84.5°C. The ultraviolet absorption spectrum indicated that the persistent impurity had been removed. After standing under vacuum for a short period the crystals again turned light yellow. The decomposition of benzanthrene will be further considered in a later section.

4. 3,4-Benzfluorene

A commercial grade sample from K & K Laboratories, Inc. was vacuum sublimed twice by Harris. He reported two fluorescences and two phosphorescences from this sample. His purified sample

was subjected to one very slow sublimation at a pressure of one atmosphere of N_2 on a cool portion of a steam table. Large, colorless single crystals were produced. This sublimation was sufficient to significantly change the absorption spectrum and remove any trace of the fluorescence reported between 4050Å and 5100Å and the phosphorescence reported between 4000 and 5000Å. The remaining emissions were also slightly altered.

5. 2,3-Benzfluorene

A commercial grade sample from K & K Laboratories, Inc. was vacuum sublimed by Harris. He reported five emissions from this compound. Vacuum entrainment sublimation was successful in removing some further impurities from this compound and left it in the form of light yellow plates. The product of this sublimation was dissolved in CCl_4 and subjected to chromatography on a very slightly activated alumina column. The first product in the effluent was shown by ultraviolet absorption spectra to be pure 2,3-benzfluorene. The first fraction was followed by a mixture of compounds. The pure 2,3-benzfluorene exhibited only one fluorescence and one phosphorescence.

6. 1,2,7,8-Dibenzfluorene

A sample of this compound was supplied by

Professor R.H. Martin of the Université Libre de Bruxelles.

7. 3,4,5,6-Dibenzfluorenone

A sample of this compound was supplied by Professor R.H. Martin of the Université Libre de Bruxelles.

8. 3,4,5,6-Dibenzfluorene

This compound was prepared by a procedure described by Martin.[36] 0.164 g. of 3,4,5,6-dibenzfluorenone and 3 ml. of 85% hydrazone hydrate were deoxygenated in a tube by freeze pumping at 77°K and the tube was sealed at 77°K under vacuum. The sample tube was placed in an oven at 180°C for 14 hours. The tube was opened in a dry box and the contents were taken up in acetic acid. The solution was treated with charcoal and the product was precipitated from aqueous acetic acid. The melting point of the product was 152.5-153.0°C. Martin reported a value of 152-152.5°C. The product was recrystallized from absolute ethanol and pure white plates were obtained.

C. Spectral Measurements

1. Absorption Spectra

Absorption spectra were recorded by means of a Cary Model 14 recording spectrophotometer. Sample cells were

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[36] R.H. Martin, J. Chem. Soc., 683 (1941).

rectangular or cylindrical matched cells of quartz or suprasil; path lengths varied from 1 mm. to 10 cm. All the cells were either those of the Beckman series or those of the Aminco Q-sharp matched series. The temperature in the sample compartment was not vigilantly controlled during absorption measurements. The temperature of the sample solutions was the same as that of their surroundings. At most times, however, the room temperature was thermostated between 22°C and 26°C. Spectra recorded under these conditions will be referred to as spectra recorded at ambient temperature.

The Cary 14 was also used with minor modification to record absorption spectra at 77°K. The sample stage was removed and a suprasil dewar containing liquid nitrogen and the sample cell was placed in the light path. The dewar was supported by a plate constructed to fit the top of the sample compartment. The sample compartment was flushed with dry nitrogen during measurements at 77°K to keep moisture from condensing on the cold surfaces. At 77°K either Beckman rectangular quartz cells or 20mm. cylindrical cells specially constructed from quartz tubing were used. Cells containing solvent were placed in the reference beam to maintain a usable baseline. Because of slight absorption of the dewar and contraction of solvents at 77°K no

extinction coefficients were evaluated from absorption spectra taken at $77^{o}K$.

Two methods were used to obtain vapor spectra. In the measurement of most of the vapor spectra the Cary 1 m. gas absorption cell was placed in the sample compartment of the Cary 14 and it was operated in the normal absorption mode. When this technique was used, the use of compensating screens was necessary and a significant baseline correction had to be made. Alternatively, when compounds had vapor pressures which were high enough, a 10cm. cell was placed in the sample compartment and the sample stage was wrapped with heating tape. The temperature of the hot stage was easily controlled and easily monitored and essentially flat base lines were easily obtained.

2. Emission and Excitation Spectra

All emission and excitation spectra were recorded by means of the Cary 14 spectrophotometer operating in a single beam mode. In most cases excitation was provided by the light from an Osram Xenon XBO 450 watt lamp monochromatized by means of the Cary 15 double monochromator. By use of a 4 inch spherical gathering mirror the usable light from this light source is

significantly improved. Total emission spectra were excited by a front surface technique which has been previously described.[37] The intensity of ultraviolet radiation for excitation purposes was improved by removing the ultraviolet filter (Corning Glass Filter C.S. 7910) which is located at the light tube exit from the lamp compartment.

A Becquerel rotating disc phosphoroscope was used to isolate the phosphorescences that were recorded. The chopper speed was controlled by a variable speed motor. Phosphorescence excitation was accomplished by one of two means. In the case of a few phosphorescence the light of the Xenon lamp passed through the Cary 15 monochromator produced sufficient light intensity for excitation. More often the phosphorescence emissions were induced by appropriately filtered radiation from a 1,000 watt General Electric A-H6 high pressure mercury arc. The Cary 14 spectrophotometer was used in the same mode for recording phosphorescence and total emissions. Again the experimental arrangement was essentially the same as that described by Holloway.

The moisture content of the purified solvents was

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[37] H.E. Holloway, op. cit., p.30.

controlled by drying them with Safe Sodium (a commercially available Na-Pb alloy). Solvents were distilled on a vacuum line from the compartment containing solvent and alloy to the sample cells. All sample solutions were prepared immediately before spectral measurements were made. Sample solutions for emission studies were diligently degassed by the freeze-pump technique and sealed immediately prior to use. In the case of studies on solutions at 77^{o}K the samples were cooled for at least 15 minutes to insure a maximum and uniform viscosity in the resulting glass before measurements were made. No attempt was made to correct emission spectra for instrument artifacts and phototube response that may vary with wavelength.

CHAPTER III

EXPERIMENTAL RESULTS AND PRELIMINARY DISCUSSION

A. The Spectra of 1-Phenylnaphthalene

The absorption and emission spectra of 1-phenylnaphthalene have been reported recently by Harris.[38] Since 1-phenylnaphthalene is one of the parent compounds of the series studied in this work its electronic states have been restudied. The absorption spectrum reported by Harris appears to be in poor agreement with that reported by Jaffé.[39] The recent findings of Holloway[40] cast doubt on the emission spectra, including multiple fluorescences and phosphorescences reported by Harris. It was felt that the number of emissions reported for the molecule indicated that it was impure. This author was never able to reproduce Harris' absorption spectrum from any sample of 1-phenylnaphthalene available, in any solvent. It seems likely that a mistake was made in the preparation of his absorption spectrum for his dissertation. The solution absorption spectra of 1-phenylnaphthalene produced

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[38] James Harris, loc. cit.

[39] H.H. Jaffé and Milton Orchin, Theory and Applications of Ultraviolet Spectroscopy, John Wiley and Sons, Inc., New York, N.Y., 1962.

[40] H.E. Holloway, loc. cit.

in this work are in general agreement with those reported by Jaffé.

Two commercial samples of 1-phenylnaphthalene were available, one from K & K Laboratories and one from Columbia Chemical Co. Many attempts were made to purify these samples. 1-Phenylnaphthalene is a thick liquid which cannot be made to crystallize under the severest of conditions. When attempts are made to chromatograph it on even reasonably active columns significant rearrangement to 2-phenylnaphthalene occurs. Attempts were made to purify 1-phenylnaphthalene on a charcoal column and by paper chromatography using various solvents. No changes were apparent in the emission spectra after these purification attempts. Several vacuum distillations were carried out on the commercial samples. Although the middle fraction of the last distillation showed emission spectra slightly different from the other fractions, the differences were not large compared with the precision resulting from the noise level in the spectra. It is likely that both commercial samples were derived from distillation of coal tar.

Synthetic 1-phenylnaphthalene was prepared and purified in the manner described in the experimental section. The vapor absorption spectrum and a solution absorption spectrum

from 3-MP solution at ambient temperature are shown in Figure 2. The absorption spectrum from absolute methanol solution at ambient temperature and the absorption spectrum from EPA solution at 77°K are shown in Figure 3. Absorption frequencies from the vapor spectrum and from the solution spectrum in EPA at 77°K are given in Table I. The fluorescence spectrum from 3-MP solution and the phosphorescence spectrum from 3-MP solution both monitored at 77°K are shown in Figure 4. The fluorescence and phosphorescence emission frequencies are given in Table 2. The 1-phenylnaphthalene emission denoted as emission G. and monitored from a 3-MP solution at 77°K in the total emission mode is shown in Figure 4. The emission frequencies for emission G. are also given in Table II. The emission spectra of the synthetic sample show significant differences from those reported by Harris. In this work a highly structured fluorescence was recorded in the region 3300-3800Å and a phosphorescence was recorded that has vibrational bands at 5000 and 5030Å. The phosphorescence is slightly more energetic than that reported by Harris. The emission found by Harris at wavelengths between 3850 and 4500Å was easily reproduced from any sample. This emission is denoted as emission G.

Emission G. was observable at room temperature from

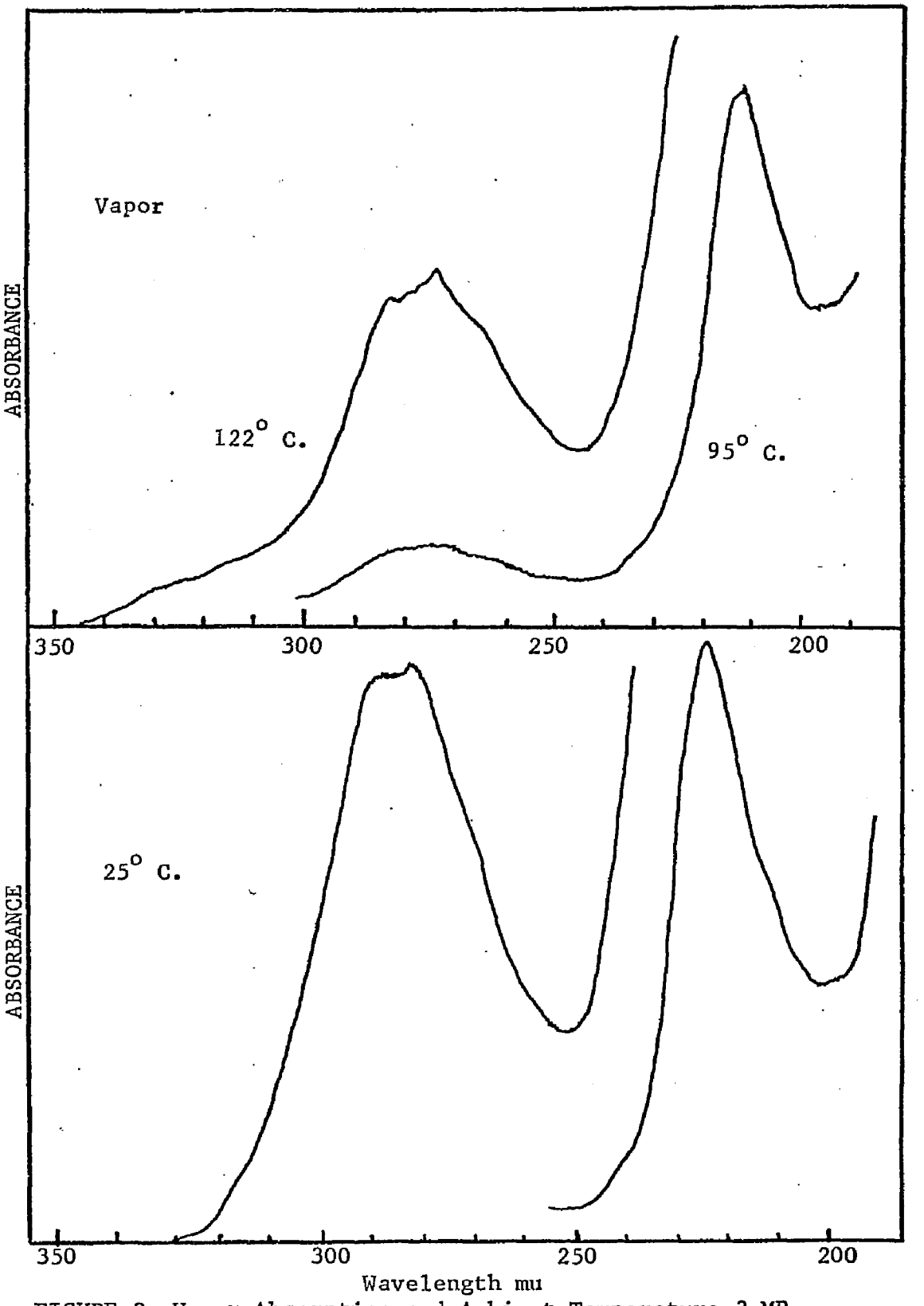

FIGURE 2. Vapor Absorption and Ambient Temperature 3-MP Solution Absorption of 1-Phenylnaphthalene.

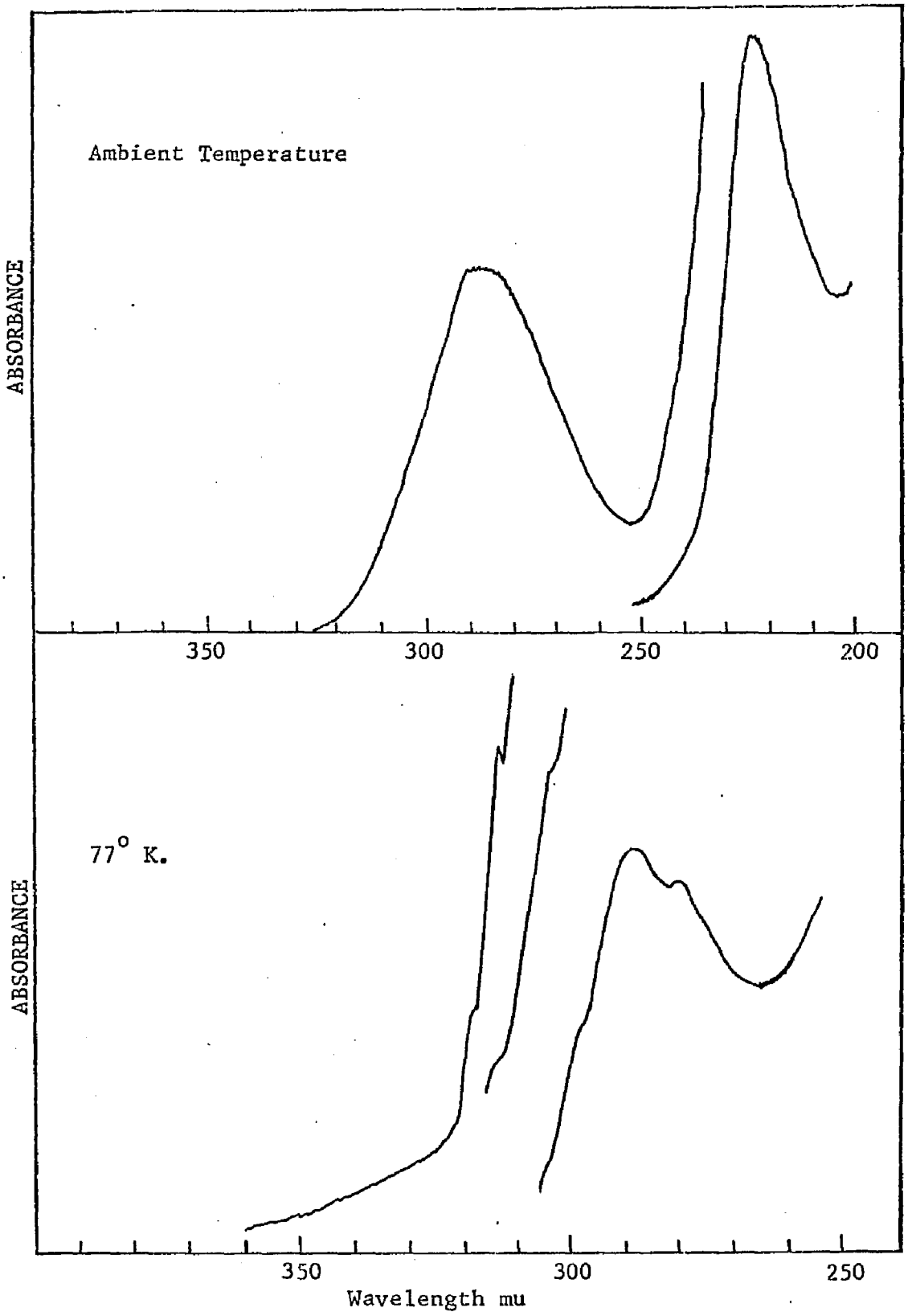

FIGURE 3. Ambient Temperature Methanol and 77° K. EPA Solution Absorptions of 1-Phenylnaphthalene.

TABLE I

Absorption Frequencies of 1-Phenylnaphthalene

Vapor Spectrum

Å	cm^{-1}	$\Delta\nu$
3300 (?)	30,300	0
3160 (?)	31,650	1,350
2830	35,335	0
2793	35,800	565
2740	36,500	1,265
2640	37,880	2,545
2140	46,730	0

$77^{\circ}K$ From EPA Solution

Å	cm^{-1}	$\Delta\nu$
3192	31,330	0
3140	31,845	515
3055	32,735	1,405
2971	33,570	2,240
2886	34,660	0
2800	35,715	1,055

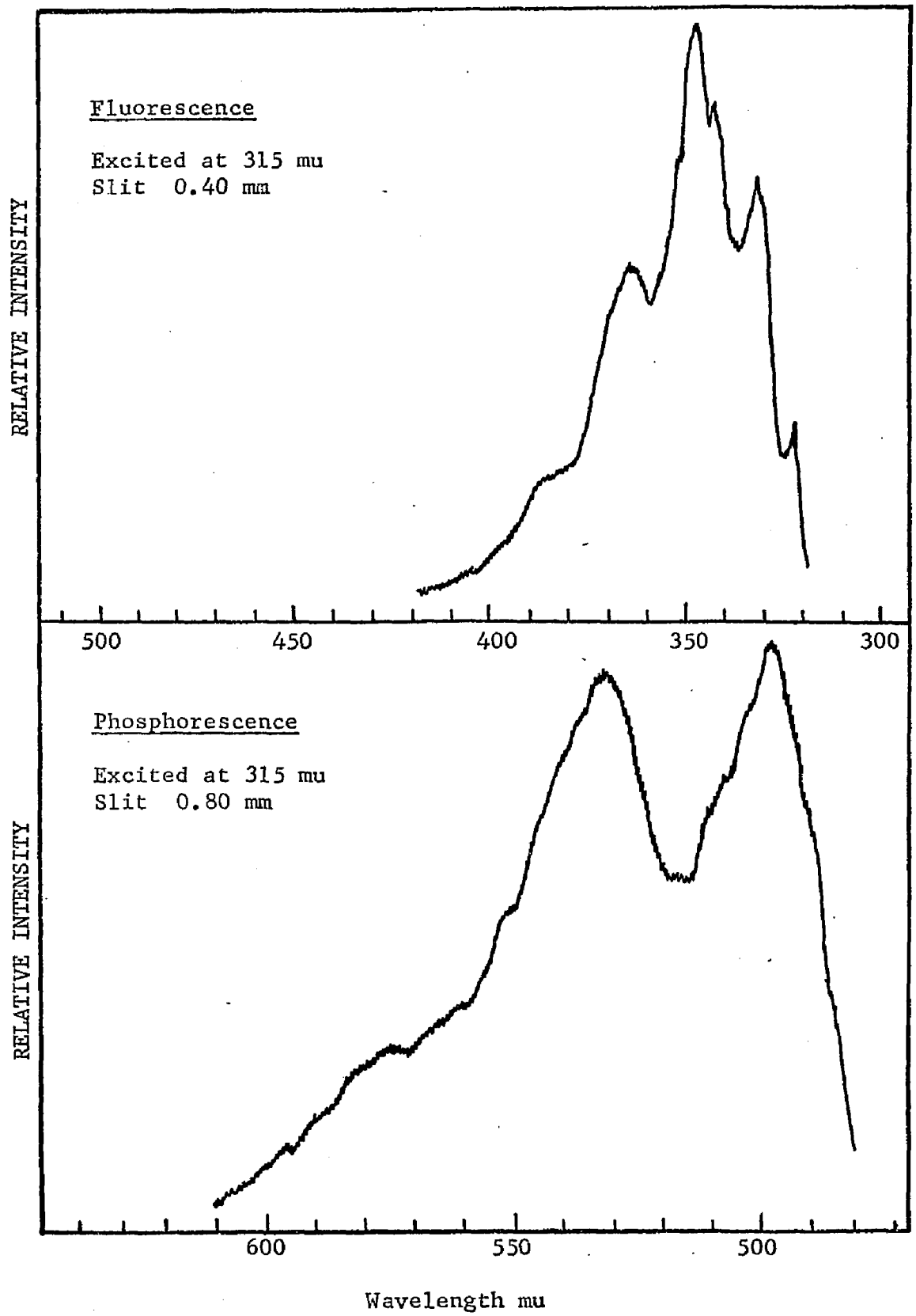

FIGURE 4. Fluorescence and Phosphorescence at 77° K. from 3-MP Solution of 1-Phenylnaphthalene.

TABLE II

Emission Frequencies of 1-Phenylnaphthalene
From 3-MP Solution at 77°K

Fluorescence

Å	cm^{-1}	$\Delta\nu$
3225	31,008	0
3320	30,120	888
3434	29,154	1,854
3480	28,736	2,272
3650	27,397	3,611
3850	25,974	5,034

Phosphorescence

Å	cm^{-1}	$\Delta\nu$
4980	20,080	0
5325	18,780	1,300

Emission G

Å	cm^{-1}	$\Delta\nu$
3810	26,250	0
4000	25,000	1,250
4220	23,700	2,550
4420	22,625	3,625

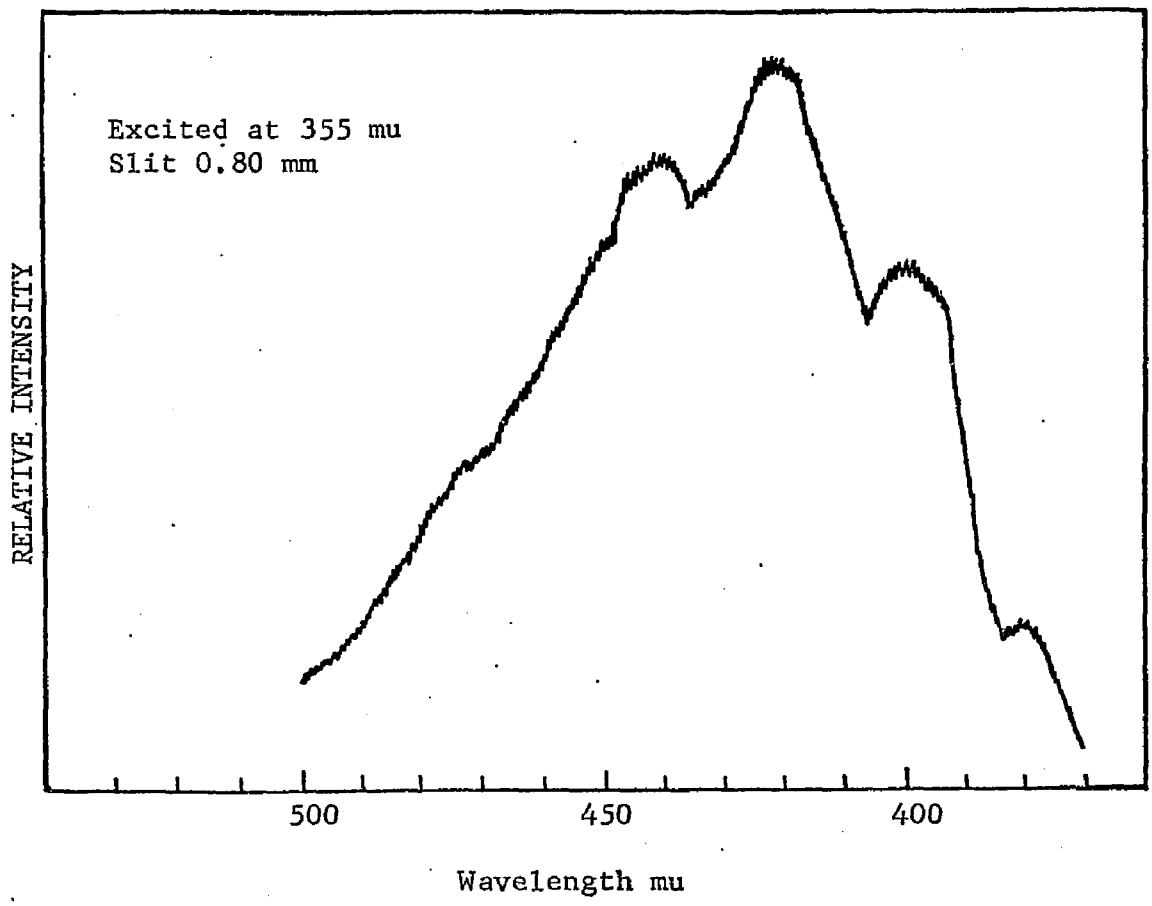

FIGURE 5. 1-Phenylnaphthalene, Emission G. Monitored at 77° K. from 3-MP Solution.

hydrocarbon solvents; it appears on the low energy side of the fluorescence. The same emission also appeared from hydrocarbon, EPA and mixed alcoholic solutions at 77°K when the total emission or the phosphorescence was observed. It appeared at the low energy side of the fluorescence or at the high energy side of the phosphorescence. This emission is most easily observed by excitation at wavelengths between 3200 and 3550Å where the other emissions of 1-phenylnaphthalene are only weakly stimulated if stimulated at all. A hydrocarbon solution of the purified synthetic product at 77°K excited at 3150Å yields a $\phi F/\phi P = 19.9$ from integration of the emission curves. Identical solutions of 1-phenylnaphthalene from commerical sources and from the purified synthetic sample were prepared in hydrocarbon solvents. At 77°K the fluorescence and emission G from each solution were carefully recorded under identical conditions. The following quantity was evaluated by integration of the emission curves:

$$\frac{\phi G/\phi F \text{ commercial}}{\phi G/\phi F \text{ synthetic}} \cong 6$$

The same lowering of intensity of G was observed by comparison with the phosphorescence from hydrocarbon solvents. Experiments

with other solvents gave similar results. It is concluded from this evidence that emission G arises from an impurity in the samples of 1-phenylnaphthalene. The author, despite concerted efforts, was never able to further reduce the intensity of emission G.

Since it is concluded that emission G arises from a species other than 1-phenylnaphthalene, natural curiosity demands that further consideration be given this fleeting species. The only available clues are the emission spectra and the evidence that species G must either be physically very similar to 1-phenylnaphthalene or show a great chemical affinity for it. The possibility of separating pure G from the mixture is a hopeless task. It will be recalled that NMR spectra indicated that there was a small concentration of aliphatic hydrogens in the sample. The assumption that the compound containing the aliphatic hydrogens gives rise to emission G is tempting, however no direct evidence is available. The emission from species G shown in Figure 5 was obtained from the synthetic sample in a hydrocarbon solution. Excitation was at 3550Å, Emission G, although weaker in the synthetic sample, showed much better vibrational resolution than do spectra from the commerical samples. It is likely that there are fewer

compounds or lower concentrations giving rise to the emission in region G in the synthetic sample than in the commercial ones. It must be concluded that emission G is a fluorescence because it is observable in hydrocarbon solvent at ambient temperature. From comparison, with known spectra it can be stated that emission G does not arise from predicted impurities such as 2-phenylnaphthalene, fluoranthene, 2,3-benzbiphenylene, or any of the benzfluorenes. In the absorption spectrum of 1-phenylnaphthalene in 3-MP solution at ambient temperature in Figure 2 the $^1A \rightarrow {}^1L_b$ transition appears as a structureless shoulder on the side of the $^1A \rightarrow {}^1L_a$ transition. The $^1A \rightarrow {}^1L_a$ transition shows very slight structure with peaks at 2810 and 2900Å. The $^1A \rightarrow {}^1B_b$ transition is structureless and centered at 2240Å. The same vapor absorption spectrum shown in Figure 2 is obtained from vapor in a five cm. quartz cell on a hot stage or in the Cary one meter gas cell. In the vapor spectrum the $^1A \rightarrow {}^1L_b$ band is red shifted while the $^1A \rightarrow {}^1L_a$ and the $^1A \rightarrow {}^1B_b$ transitions are blue shifted. The positive absorption between 3100Å and 3400Å is attributed to the $^1A \rightarrow {}^1L_b$ transition. Slight vibrational maxima are indicated at 3160 and 3300Å. The blue shifted $^1A \rightarrow {}^1L_a$ transition at 122°C now shows considerable vibrational structure. At 95°C the $^1A \rightarrow {}^1B_b$ transition remains structureless and is centered

at 2140Å. The extinction coefficients were evaluated for the $^1A \rightarrow {}^1L_a$ transition (8,100 1./m.cm.) and the $^1A \rightarrow {}^1B_b$ transition (55,000 1./m.cm.). It is impossible to obtain an absorption spectrum of 1-phenylnaphthalene at 77°K in hydrocarbon solutions either in one centimeter cells or in two centimeter quartz tubes. Precipitation of particles which scatter badly takes place. Figure 3 shows the results of several attempts to obtain the absorption spectrum of EPA solutions at 77°K in two centimeter test-tubes. Although the solution at 77°K appears clear some scattering still takes place. It is thought that the bands and shoulders at 3192Å, 3140Å, 3055Å, and 2971Å belong to the $^1A \rightarrow {}^1L_b$ transition and are superimposed on the $^1A \rightarrow {}^1L_a$ transition which shows vibrational peaks at 2886 and 2800Å.

For the present discussion emission G. will not be considered to be that of the 1-phenylnaphthalene molecule. It is recognized that the fluorescence and phosphorescence may be somewhat perturbed because the samples are in an impure state. Nevertheless it will be assumed that the spectra in Figure 3 are characteristic of the species, 1-phenylnaphthalene. The phosphorescence is considered to be typical of an emission originating from a ^3L_a state. The fluorescence of 1-phenyl-naphthalene shows considerable structure and is considered to

be typical of a $^1A \leftarrow {}^1L_b$ transition.

The fact that vibrational structure is observable both in absorption and emission spectra at 77°K implies that a high population of molecules with a fixed equilibrium angle between phenyl and naphthyl rings exists both in the ground and ^1L_b excited states. Holloway[41] has predicted that the energy of the $^1A \rightarrow {}^1L_b$ transition as well as that of the $^1A \rightarrow {}^1L_a$ transition will be a function of the angle between the rings of 2-phenylnaphthalene. If a significant distribution of molecules with different angles between rings exists, it would be expected that all fine structure would be lost due to the superposition of many transitions of slightly different energies. Holloway concluded that the potential energy curve for the 2-phenylnaphthalene ground state exhibited two minima; one corresponding to a planar configuration and the other corresponding to an angle between rings of 35°-40°. He also concluded that the ^1L_b excited state was planar and had a potential energy curve exhibiting only one minimum.

This clearly cannot be the case for 1-phenylnaphthalene.

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[41] H.E. Holloway, ibid.

The potential energy curve with respect to ring rotation will be defined by the sum of two competing energetic factors. The first factor is the tendency toward planarity due to the p_z orbital overlap across the bond between rings. The competing process is the tendency toward nonplanarity because of the steric repulsions of the 9-12 and the 2-16 hydrogens. Because of the geometry of the molecule the repulsion energy due to the overlap of the 9-12 hydrogens must become very large as the rings become coplanar. Because of this fact, there can be no possibility for an energy minimum either in the ground state or in the ^1L_b excited state in the planar configuration of 1-phenylnaphthalene. In the theoretical section the molecule will be further considered. The concepts treated qualitatively here will be given a quantitative basis.

B. The Spectra of 3,4,5,6-Dibenzfluorene

Microwave studies of fluorene indicate that it is planar within experimental error.[42] All the benzfluorenes and dibenzfluorenes are compounds that are presumed, as a first approximation, to be planar.

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[42] D.M. Burns and J. Iball, Proc. Roy. Soc., A227, 200 (1955).

If 3,4,5,6-dibenzfluorene were planar it would have C_{2v} symmetry. However models show that the 12- and 13-hydrogens are subject to severe repulsion. It is likely that the naphthalene rings remain nearly planar and are rotated with respect to each other about the fusing bond with the methylene bridge suffering most of the distortion from ideal bond angles. The amount of rotation of the rings with respect to each other must be the result of a summation of the energy lost because of rotation of the naphthalene pi-clouds away from co-planarity and the energy gained by lowering of the repulsion energy between the interferring hydrogens.

The absorption spectra of 3,4,5,6-dibenzfluorene in 3-MP solution at ambient temperature and in IPMP solution at 77°K are shown in Figure 6. The transition frequencies observed in the absorption spectra are given in Table III. The fluorescence and phosphorescence spectra from IPMP solutions at 77°K are shown in Figure 7. The emission transition frequencies are given in Table IV.

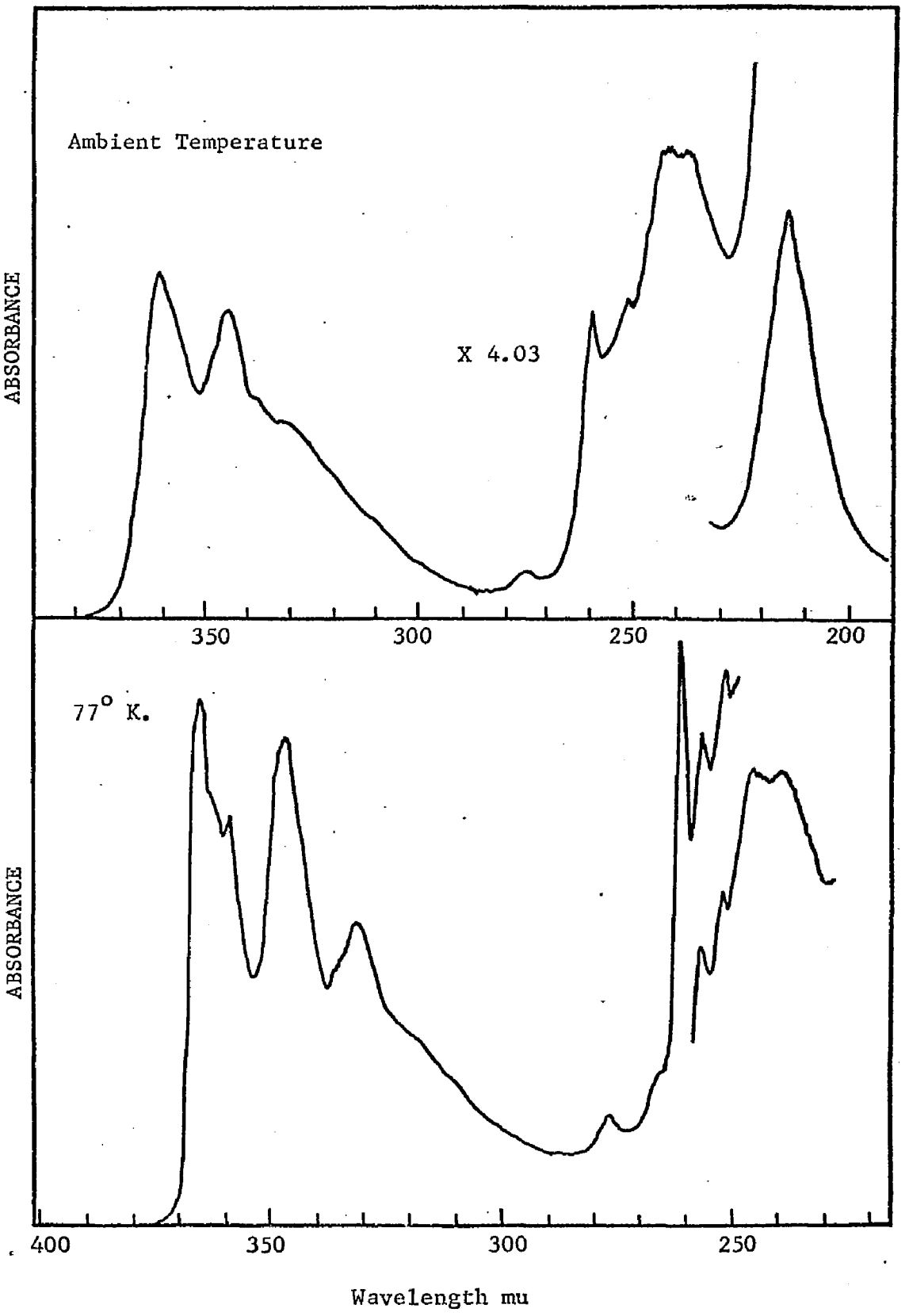

FIGURE 6. Ambient Temperature and 77°K. Absorptions of 3,4,5,6-Dibenzfluorene from 3-MP and IPMP Solutions.

TABLE III

Absorption Frequencies of 3,4,5,6-Dibenzfluorene

Ambient Temperature from 3-MP Solution

Å	cm^{-1}
3602	27,762
3445	29,028
3377	29,612
3308	30,230
2750	36,364
2600	38,462
2515	39,761
2432	41,118
2387	41,896
2152	41,468

$77^{\circ}K$ From IPMP Solution

Å	cm^{-1}	$\Delta\nu$
3655	27,360	0
3626	27,578	218
3593	27,832	472
3472	28,802	1,442
3319	30,130	2,770
2774	36,049	0
2659	37,608	0
2617	38,212	604
2574	38,850	1,242
2530	39,525	1,917
2457	40,700	0
2400	41,667	967

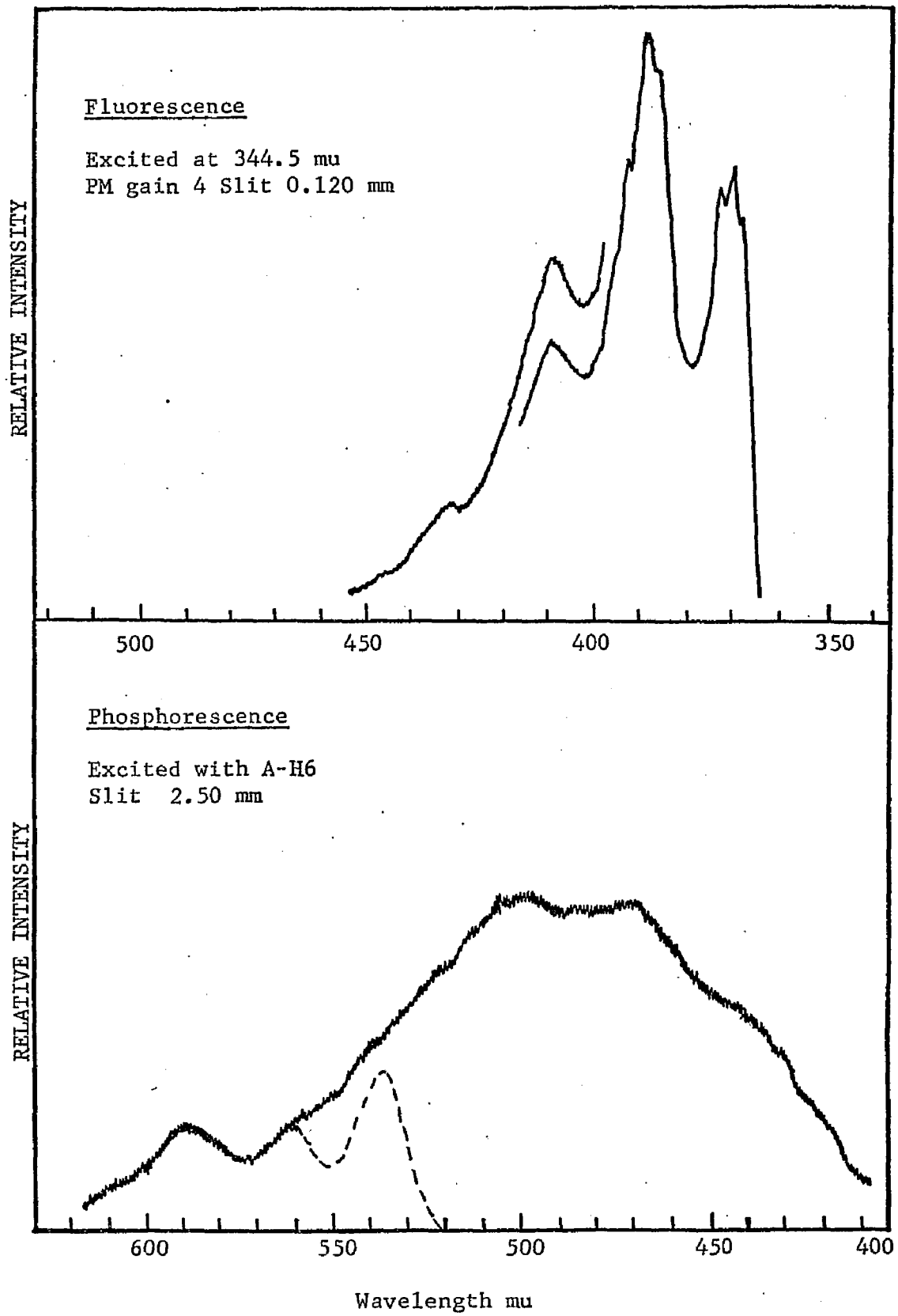

FIGURE 7. Fluorescence and Phosphorescence of.

3,4,5,6-Dibenzfluorene from IPMP Solution at 77° K.

TABLE IV

Fluorescence Frequencies of
3,4,5,6-Dibenzfluorene

77°K From IPMP Solution

Å	cm^{-1}	$\Delta\nu$
3682	27,159	0
3703	27,005	154
3731	26,802	357
3863	25,887	1,272
3880	25,773	1,386
3952	25,304	1,855
4090	24,450	2,709
4320	23,148	4,011

C. The Spectra of 3,4-Benzfluorene

Models indicate the 5- and the 12-hydrogens of this compound are very near each other but do not appear to overlap as do the interferring hydrogens in 3,4,5,6-dibenzfluorene. There will be no loss of symmetry if the ring systems are rotated with respect to each other. Again there will be an energetic balance determined by rotation of the rings about the fusing bond. Since the hydrogen-hydrogen repulsion term is much smaller the angle of rotation is smaller in the case of 3,4-benzfluorene than in that of 3,4,5,6-dibenzfluorene.

The absorption spectra of 3,4-benzfluorene from IPMP solutions at ambient temperature and at 77°K are shown in Figure 8. The absorption spectrum from absolute methanol solution at ambient temperature is shown in Figure 9. The absorption transition frequencies are given in Table V. The fluorescences at 77°K from 3-MP solution and at 4°K from IPMP are shown in Figure 10 and the emission frequencies are given in Table VI. 3,4-Benzfluorene also exhibits a concentration dependent excimer emission. This excimer emission and the phosphorescence emission from 3-MP solutions at 77°K are depicted in Figure 11. The intense emission in the excimer spectrum beginning at about 5000Å is the leading edge of the

molecular phosphorescence.

It is interesting to note that only a slight improvement in the resolution of the structure of the fluorescence was observed when the temperature was lowered from 77°K to about 4°K. The resolution was not limited by the slits and optics in the Cary spectrophotometer. Although the noise level resulting from operating at high photomultiplier tube voltages was annoying it did not affect the resolution of this particular spectrum. It appears that in this case there was little increase in resolution of the vibrational structure to be gained by lowering the temperature. Whether this effect, or the lack of it, is a phenomenon which will be generally observed in emissions from hydrocarbon solutions at 4°K remains to be determined. The discovery that this mixed hydrocarbon glass can be used at 4°K is a potentially important one and further investigation of its uses should be carried out.

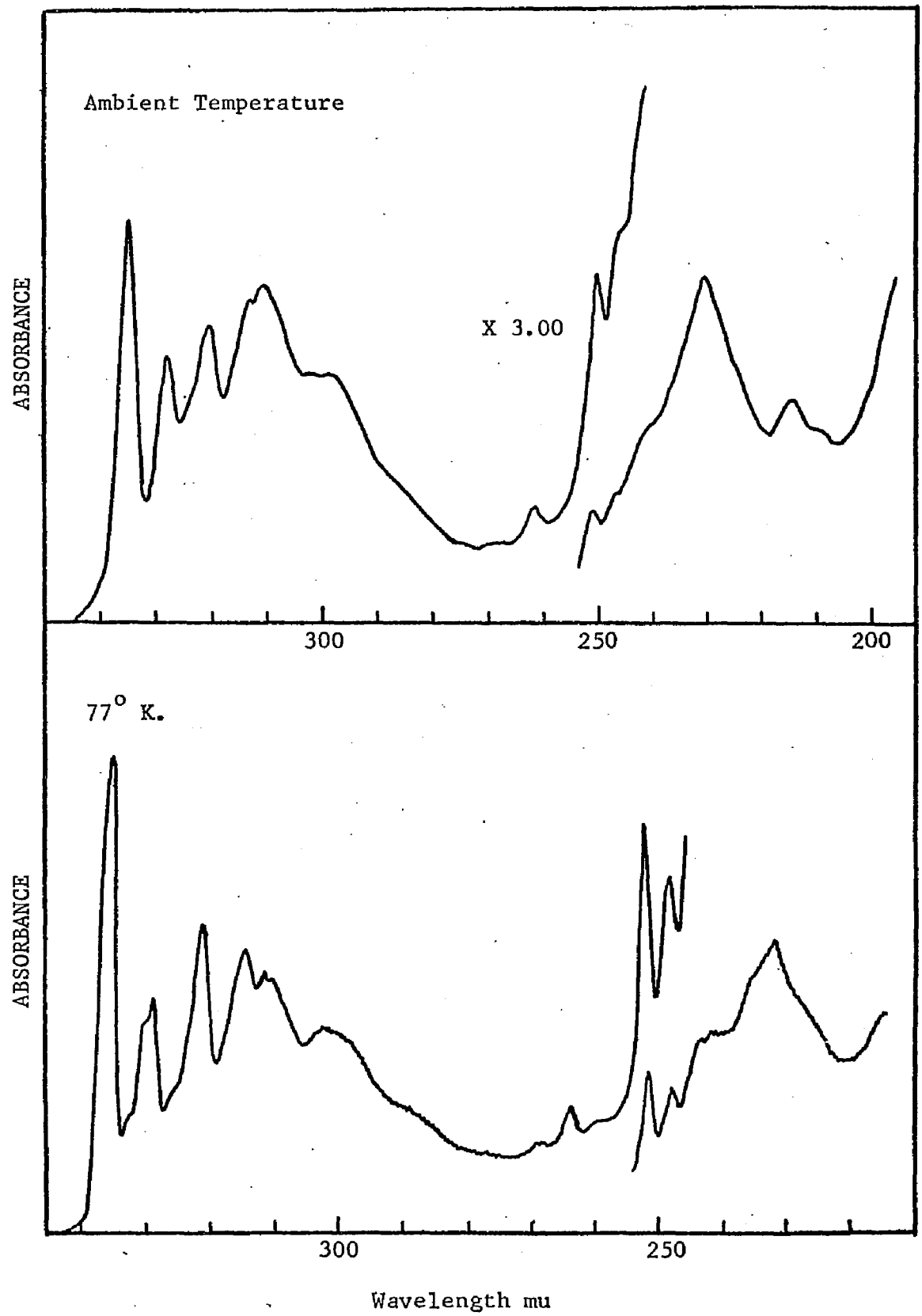

FIGURE 8. Ambient Temperature and 77° K. Absorption of 3,4-Benzfluorene from IPMP Solution.

TABLE V

Absorption Frequencies and Extinction Coefficients of 3,4-Benzfluorene

Ambient Temperature from Methanol Solution

Å	cm^{-1}	ϵ(l./m.*cm.)$\underline{x}10^{4}$
3350	29,851	1.45
3275	30,534	1.12
3110	32,154	1.53
3000	33,333	1.12
2620	38,168	0.62
2510	39,841	1.55
2320	43,103	4.67

Table V (continued)

Ambient Temperature from IPMP Solution

Å	cm^{-1}
3345	29,895
3280	30,448
3210	31,153
3135	31,898
3105	32,202
3020	33,112
2975	33,613
2680	37,313
2620	38,168
2505	39,920
2465	40,568
2400	41,667
2305	43,384
2140	46,729
2100	47,619

Table V (Continued)

77°K From IPMP Solution

Å	cm^{-1}	$\Delta\nu$
3365	29,735	0
3324	30,084	249
3301	30,294	559
3291	30,386	651
3249	30,779	1,044
3225	31,008	1,273
3214	31,114	1,379
3147	31,776	2,041
3117	32,082	2,347
3104	32,216	2,481
3014	33,178	3,443
2764	36,180	0
2684	37,258	0
2639	37,893	635
2595	38,536	1,278
2519	39,698	0
2480	40,322	624
2432	41,118	
2411	41,476	
2317	43,159	
2141	46,707	
2069	48,333	

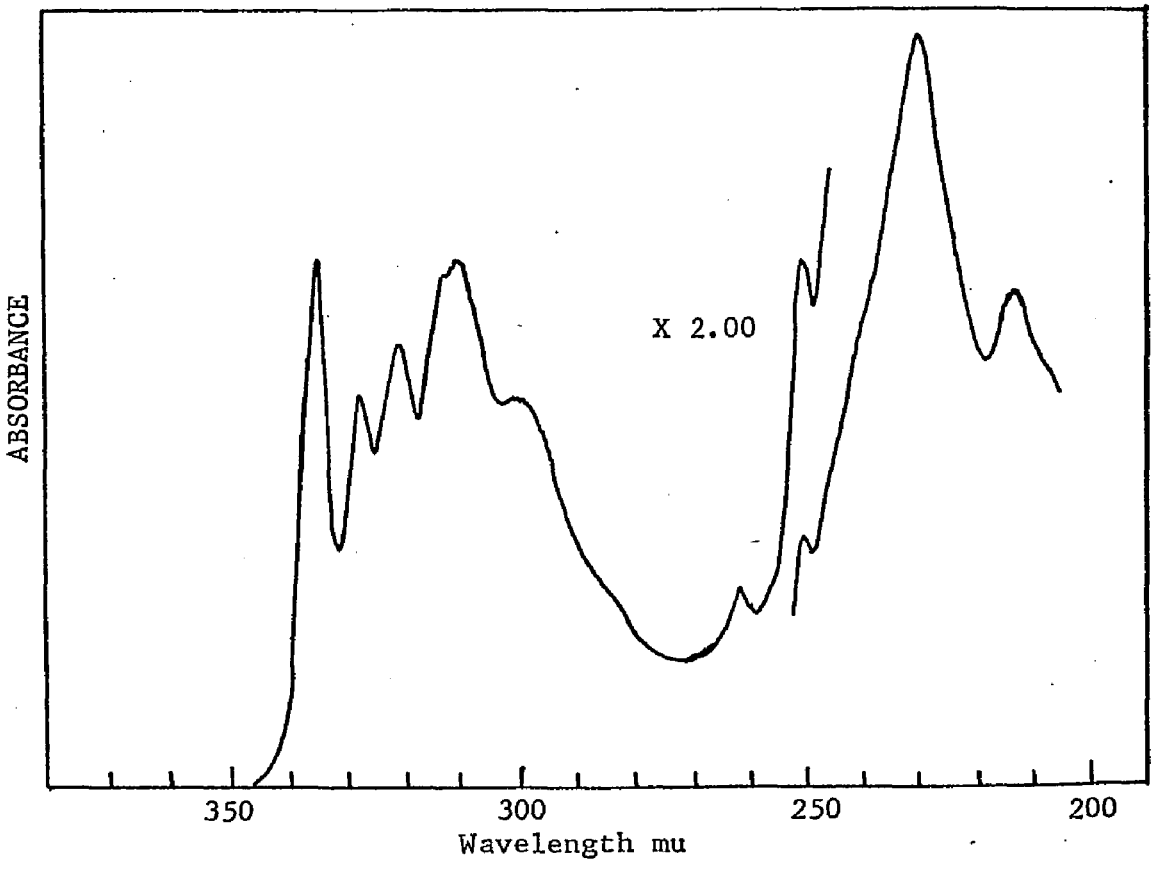

FIGURE 9. Ambient Temperature Absorption of 3,4-Benzfluorene from Methanol Solution.

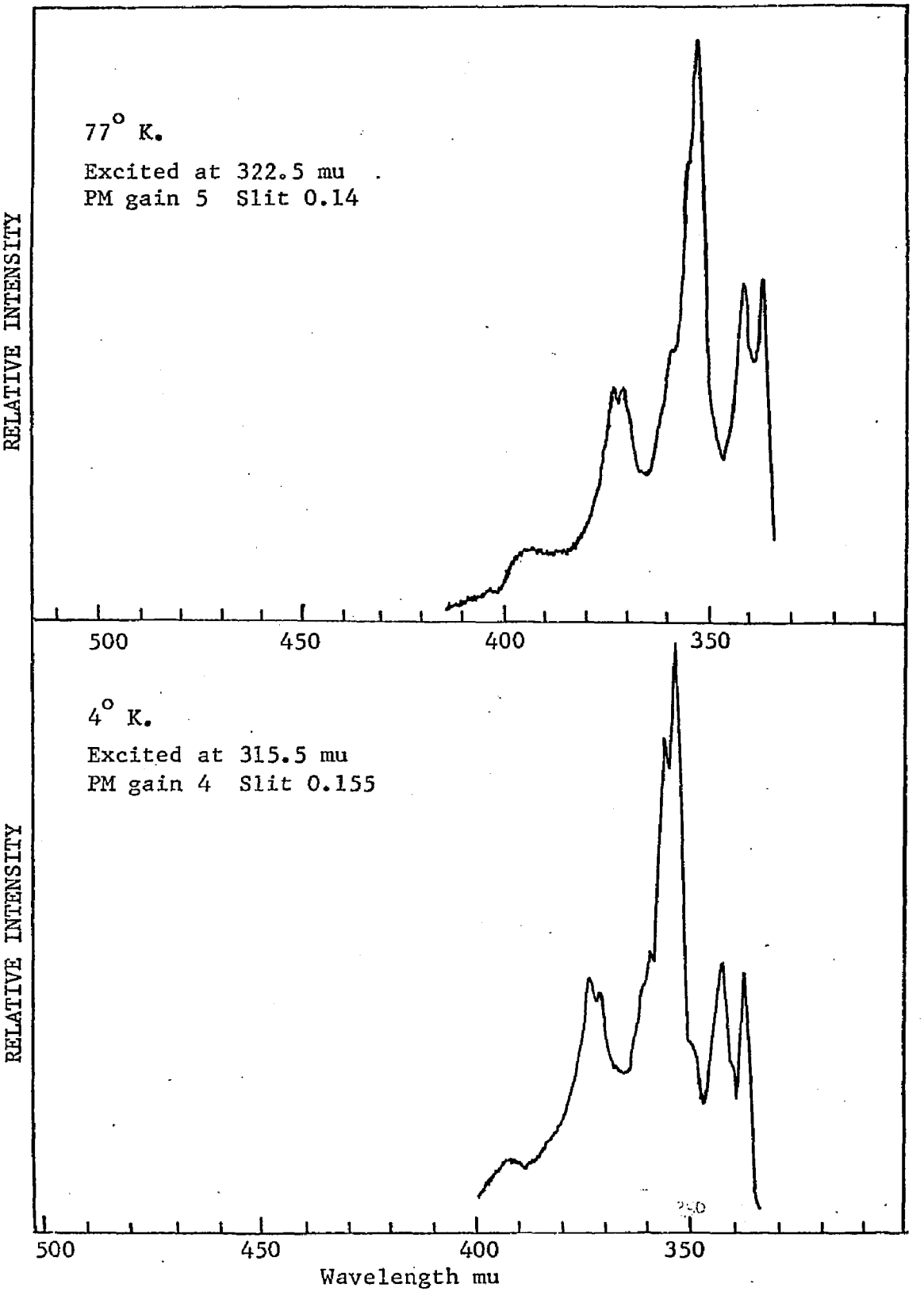

FIGURE 10. Fluorescence of 3,4-Benzfluorene from 3-MP Solution at 77° K. and IPMP Solution at 4° K.

TABLE VI

Emission Frequencies of 3,4-Benzfluorene

Fluorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3375	29,630	0
3423	29,214	416
3530	28,329	1,301
3585	27,894	1,736
3713	26,932	2,698
3735	26,774	2,856
3915	25,543	4,087

Fluorescence from IPMP Solution at 4°K

Å	cm^{-1}	$\Delta\nu$
3376	29,620	0
3424	29,206	414
3497	28,596	1,024
3530	28,329	1,291
3553	28,145	1,475
3591	27,847	1,773
3714	26,925	2,695
3737	26,759	2,861
3920	25,510	4,110

Phosphorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
5181	19,301	0
5311	18,820	472
5565	17,969	1,332
5614	17,813	1,488

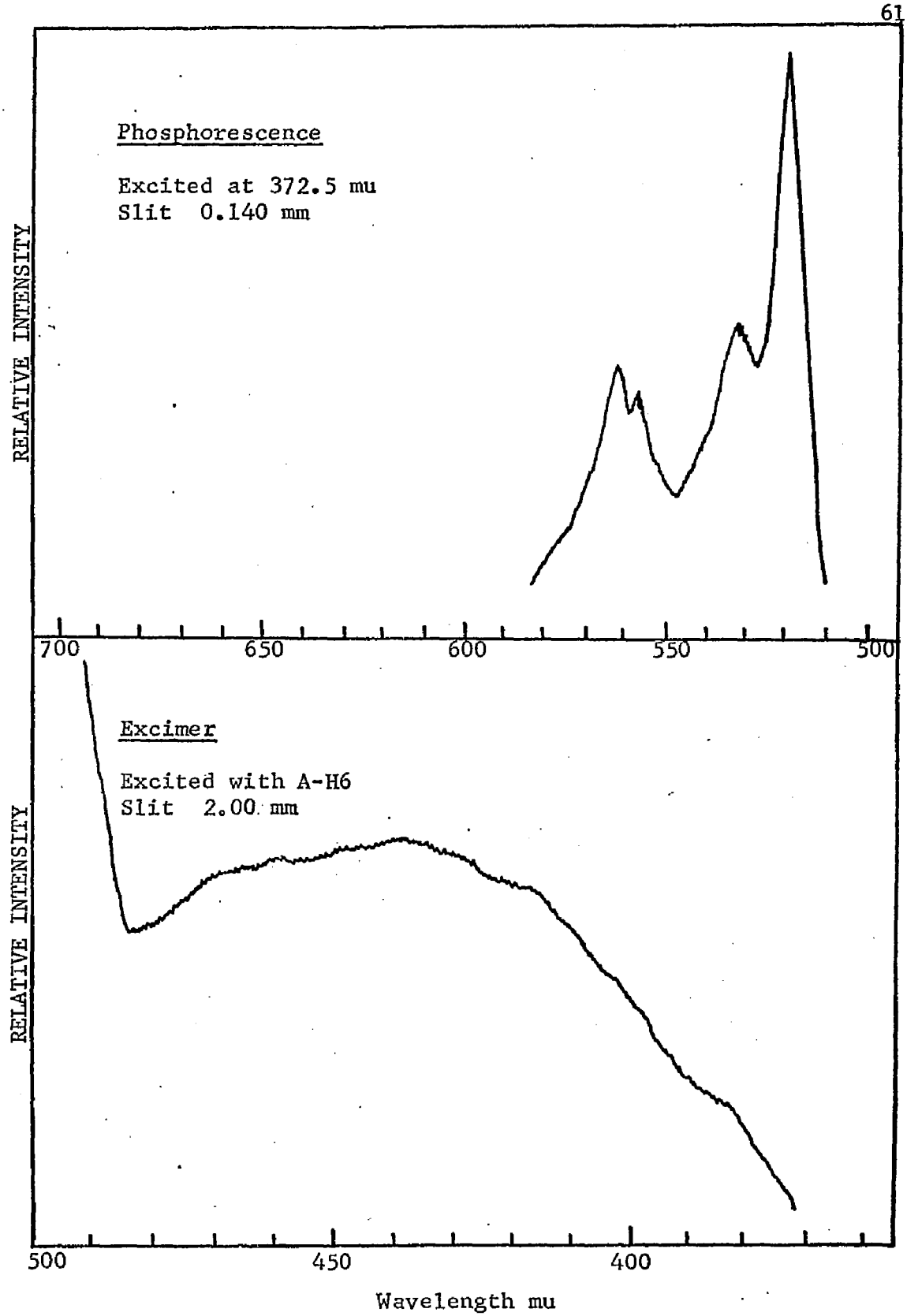

FIGURE 11. Phosphorescence and Excimer Emission of 3,4-Benzfluorene from 3-MP Solution at 77°K.

D. The Spectra of Benzanthrene

Although the 1- and 11-hydrogens are reasonably close, from models it appears that there will be little steric hindrance between them. However, the six-membered ring that contains the methylene bridge can no longer be considered to be at a minimal energy when the whole carbon skeleton lies in a plane. The methylene carbon tends to bend out of the molecular plane. When this occurs, it follows that the rings must be slightly skewed with respect to each other. If the fusing-bond length is intermediate between that of a C-C single bond and that of an aromatic C-C bond (closer to the former) the steric strain tending to force the methylene carbon out of the molecular plane will become smaller as the bonding at this carbon approaches sp^2 rather than sp^3. This should have a distinct effect on the acidity of the methylene hydrogens. Further comments on this subject will be made later. Considering the gross geometry, it can be said with assurance that the aromatic rings are slightly skewed from coplanarity in the molecular ground state.

The absorption spectra of benzanthrene in isopropanol solution at ambient temperature and in IPMP solution at $77^{\circ}K$ are shown in Figure 12. The transition frequencies and extinction

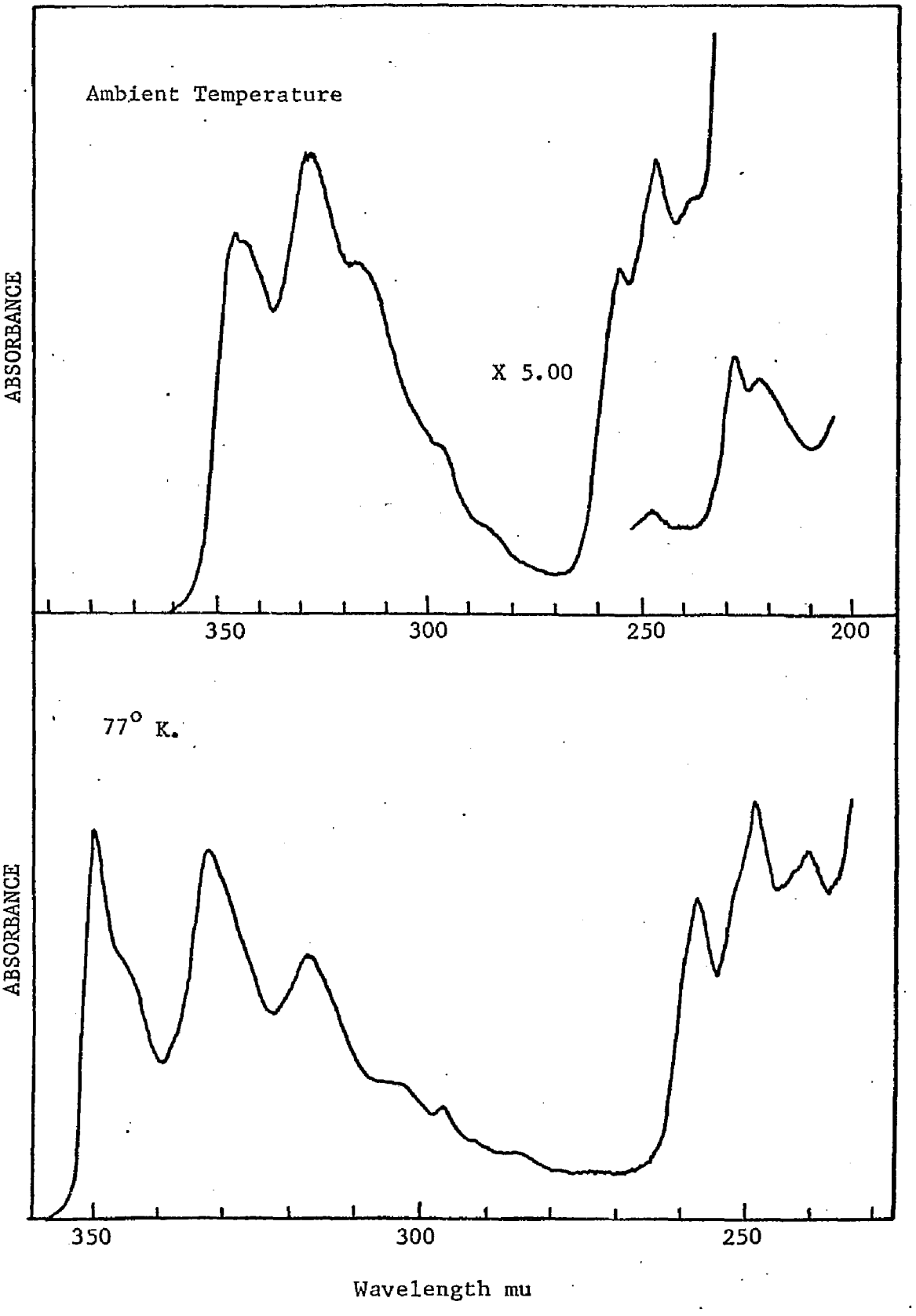

FIGURE 12. Ambient Temperature and 77° K. Absorption of Benzanthrene from isopropanol and IPMP Solutions.

coefficients are given in Table VII. The fluorescence and phosphorescence spectra of benzanthrene in 3-MP solutions at 77°K are shown in Figure 13 and the transition frequencies are given in Table VIII. Emissions of photochemical decomposition products that were monitored by means of the phosphorescence technique are shown in Figure 14. In a later section this photochemical reaction will be considered further.

E. The Spectra of 2,3-Benzfluorene

2,3-Benzfluorene suffers none of the distortions due to hydrogen repulsions that occur in the other members of this series. If fluorene is planar, 2,3-benzfluorene should also be planar.

The absorption spectra of 2,3-benzfluorene in IPMP solutions at ambient temperature and at 77°K are shown in Figure 15. The absorption transition frequencies and extinction coefficients are given in Table IX. The fluorescence from IPMP solution at 77°K is shown in Figure 16. This fluorescence is extremely structured and shows vibrational bands so narrow that the spectrum appears much like an atomic emission spectrum. The phosphorescence spectrum from IPMP solution at 77°K is also shown in Figure 16. The emission frequencies are given in Table X.

TABLE VII

Absorption Frequencies and Extinction Coefficients of Benzanthrene

Ambient Temperature from Isopropanol Solution

Å	cm^{-1}	$\epsilon(l./m.cm.)\underline{x}10^4$
3460	28,902	1.34
3437	29,095	1.31
3287	30,423	1.64
3171	31,536	1.26
2559	39,078	1.18
2472	40,453	1.57
2378	42,052	1.45
2287	43,725	1.44
2230	44,843	4.06

$77^{o}K$ From IPMP Solution

Å	cm^{-1}	$\Delta\nu$
3495	28,612	0
3460	28,901	289
3322	30,102	1,490
3170	31,546	2,934
3035	32,949	4,337
2962	33,761	0
2917	34,282	?
2849	35,100	?
2570	38,910	0
2485	40,241	1,331
2398	41,701	2,791

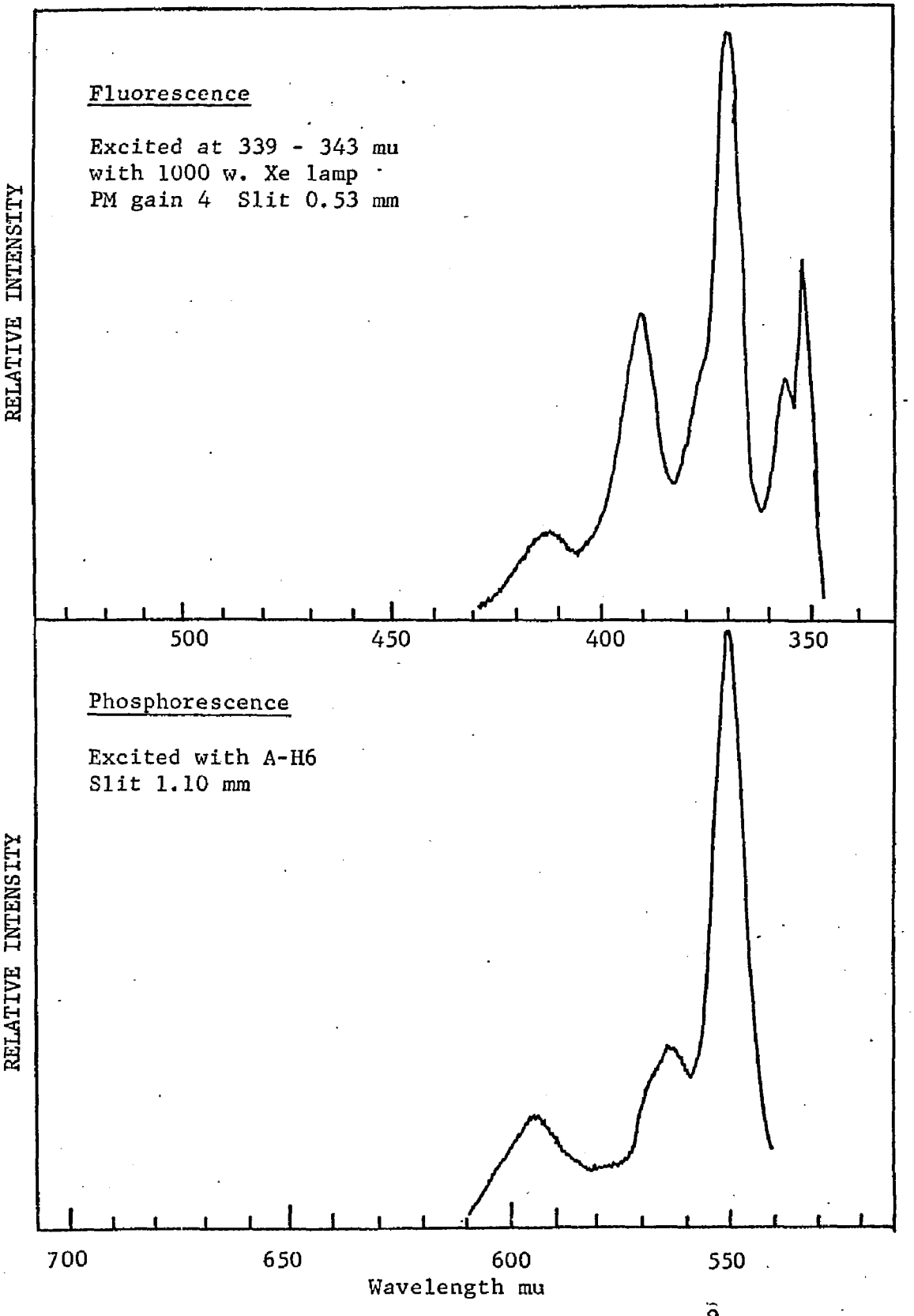

FIGURE 13. Fluorescence and Phosphorescence at 77° K. of Benzanthrene from 3-MP Solution.

TABLE VIII

Emission Frequencies of Benzanthrene

Fluorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3512	28,474	0
3561	28,082	390
3700	27,027	1,447
3903	25,621	2,853
4130	24,213	4,261

Phosphorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
5510	18,149	0
5640	17,730	419
5900	16,949	1,200

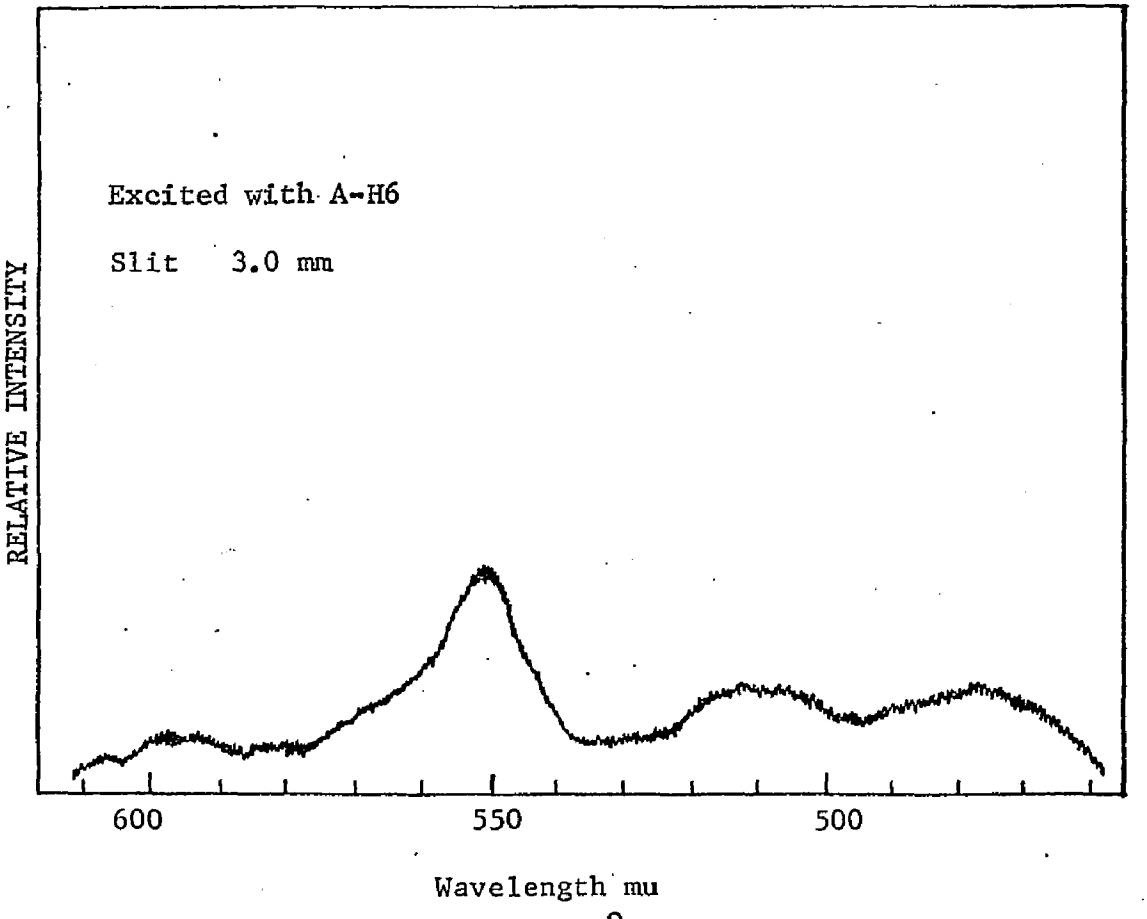

FIGURE 14. Phosphorescence at 77° K. from 3-MP Solution of Benzanthrene photodecomposition Products.

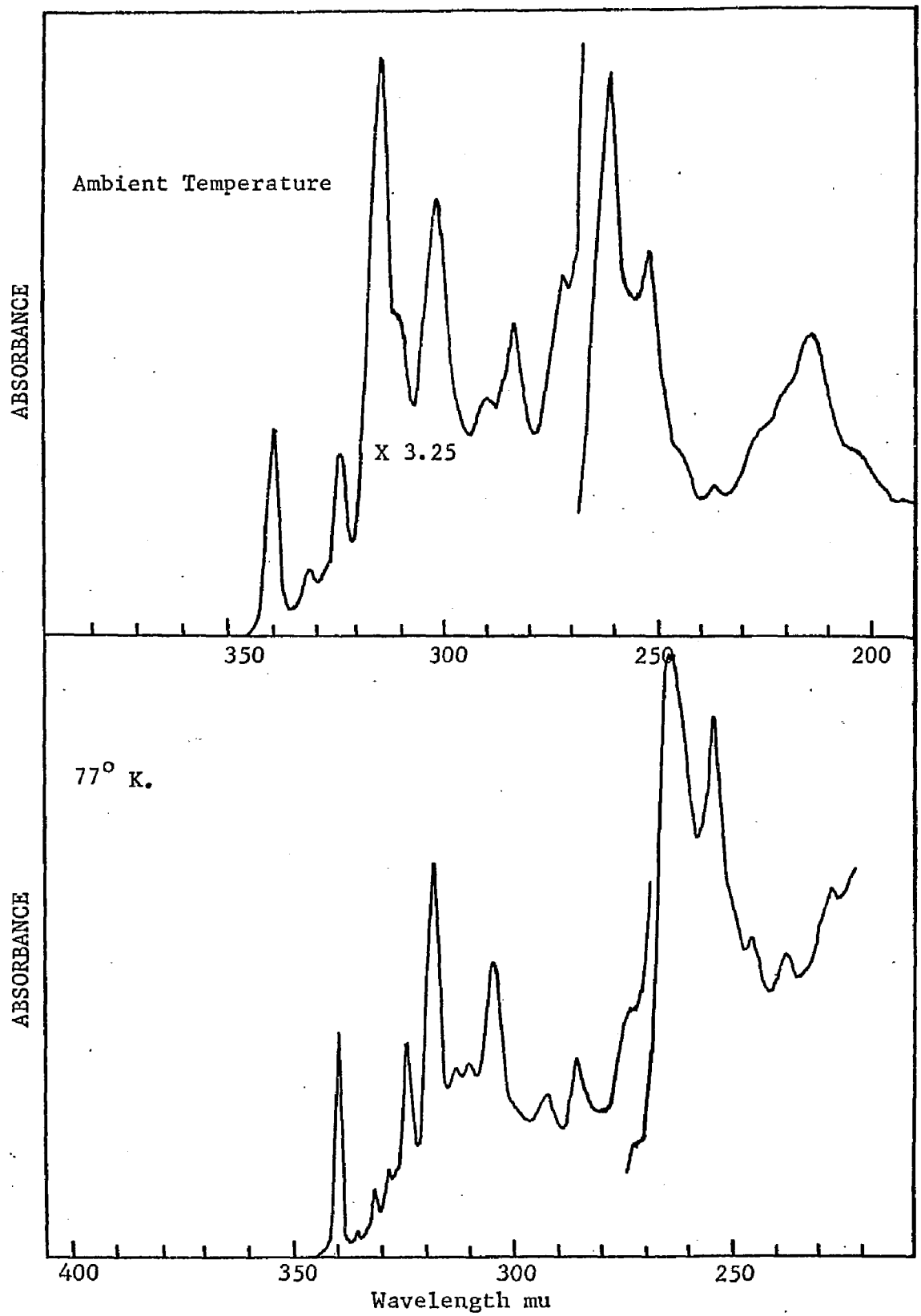

FIGURE 15. Ambient Temperature and 77° K. Absorption of 2,3-Benzfluorene from IPMP Solution.

TABLE IX

Absorption Frequencies and Extinction Coefficients of 2,3-Benzfluorene

Ambient Temperature from IPMP Solution

Å	cm^{-1}	ϵ(1./m.cm.)x10^4
3397	29,438	0.700
3315	30,166	0.239
3242	30,845	0.644
3153	31,716	2.04
3113	32,123	1.16
3021	33,102	1.58
2900	34,483	0.883
2844	35,162	1.14
2726	36,684	1.32
2623	38,124	6.95
2527	39,573	4.78
2455	40,733	2.24
2377	42,070	1.84
2251	44,425	2.65
2212	45,208	3.13
2154	46,425	3.75

Table IX (Continued)

77°K From IPMP Solution

Å	cm^{-1}	$\Delta\nu$
3397	29,438	0
3355	29,806	368
3316	30,157	719
3287	30,423	985
3245	30,817	1,379
3185	31,397	0
3136	31,888	491
3103	32,227	830
3047	32,819	1,422
3005	33,278	1,881
2927	34,165	2,768
2855	35,026	0
2730	36,630	?
2655	37,665	0
2507	39,888	2,223
2456	40,717	
2388	41,876	
2273	43,995	

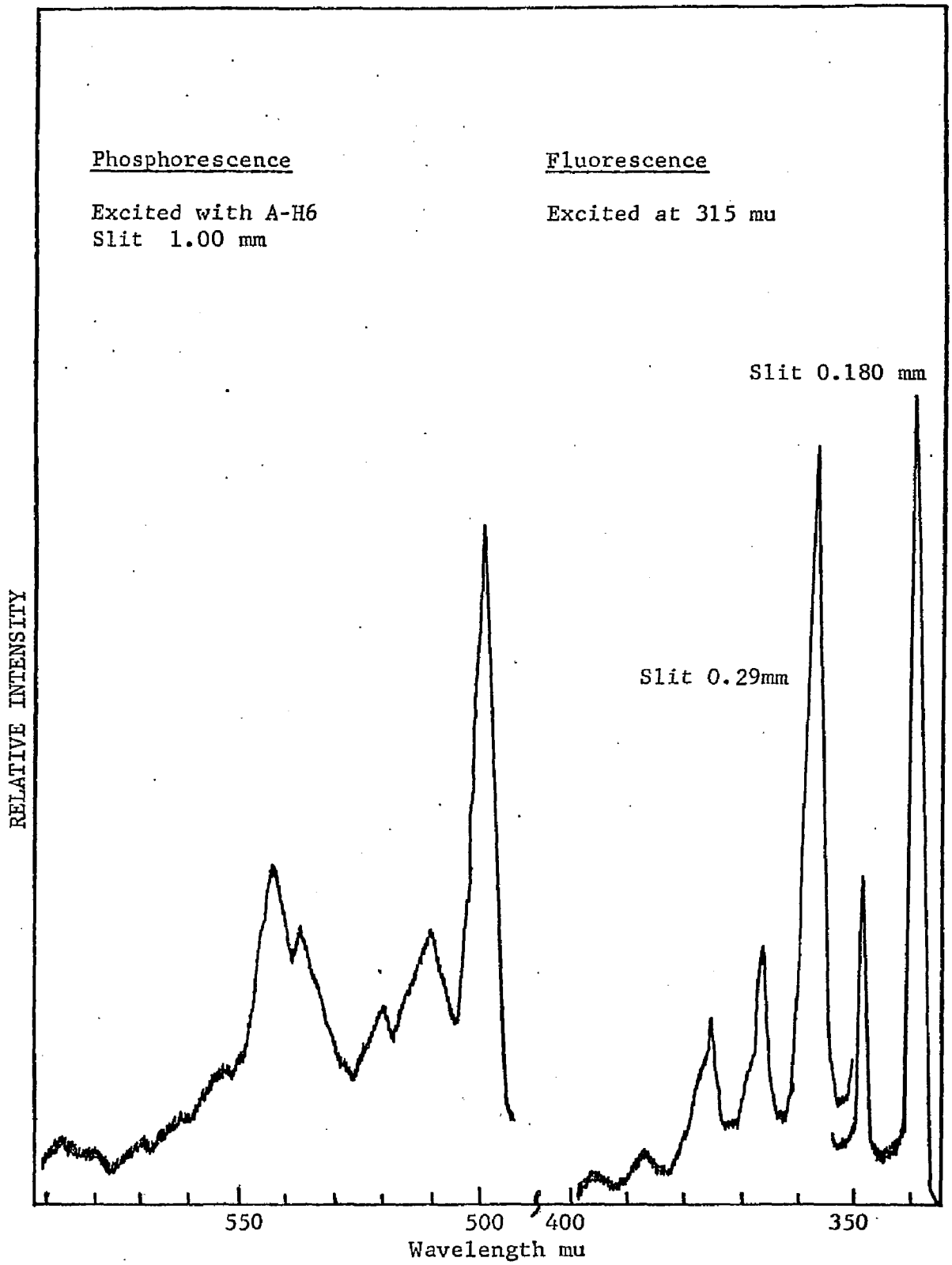

FIGURE 16. Fluorescence and Phosphorescence at 77°K. of 2,3-Benzfluorene from IPMP Solution.

TABLE X

Emission Frequencies of 2,3-Benzfluorene

Fluorescence from IPMP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3400	29,412	0
3489	28,662	750
3568	28,027	1,385
3669	27,255	2,157
3765	26,560	2,852
3875	25,806	3,606

Phosphorescence from IPMP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
4992	20,030	0
5115	19,550	580
5205	19,210	820
5368	18,630	1,400
5425	18,430	1,600

F. The Spectra of 1,2-Benzfluorene

The electronic spectra of 1,2-benzfluorene have been recently reported by Holloway.[43] Since the compound is an important member of the series studied in this work its electronic spectra are reproduced from the dissertation of Holloway. The absorption spectra of 1,2-benzfluorene in 3-MP solutions at ambient temperature and at 77°K are shown in Figure 17, and the absorption frequencies are given in Table XI. The 77°K fluorescence and phosphorescence spectra from 3-MP solutions are shown in Figure 18 and the emission frequencies are given in Table XII.

Like 2,3-benzfluorene, 1,2-benzfluorene should have no significant hydrogen-hydrogen interactions and should be planar. Unlike 2,3-benzfluorene in which the phenyl ring interacts only long-axis with the naphthalene ringe, in 1,2-benzfluorene the phenyl ring interacts long-axis with the naphthalene ring through the fusing bond and short-axis through the bridging group.

G. The Spectra of 2-Phenylnaphthalene

Holloway has also reported the electronic properties

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[43] H.E. Holloway, loc. cit.

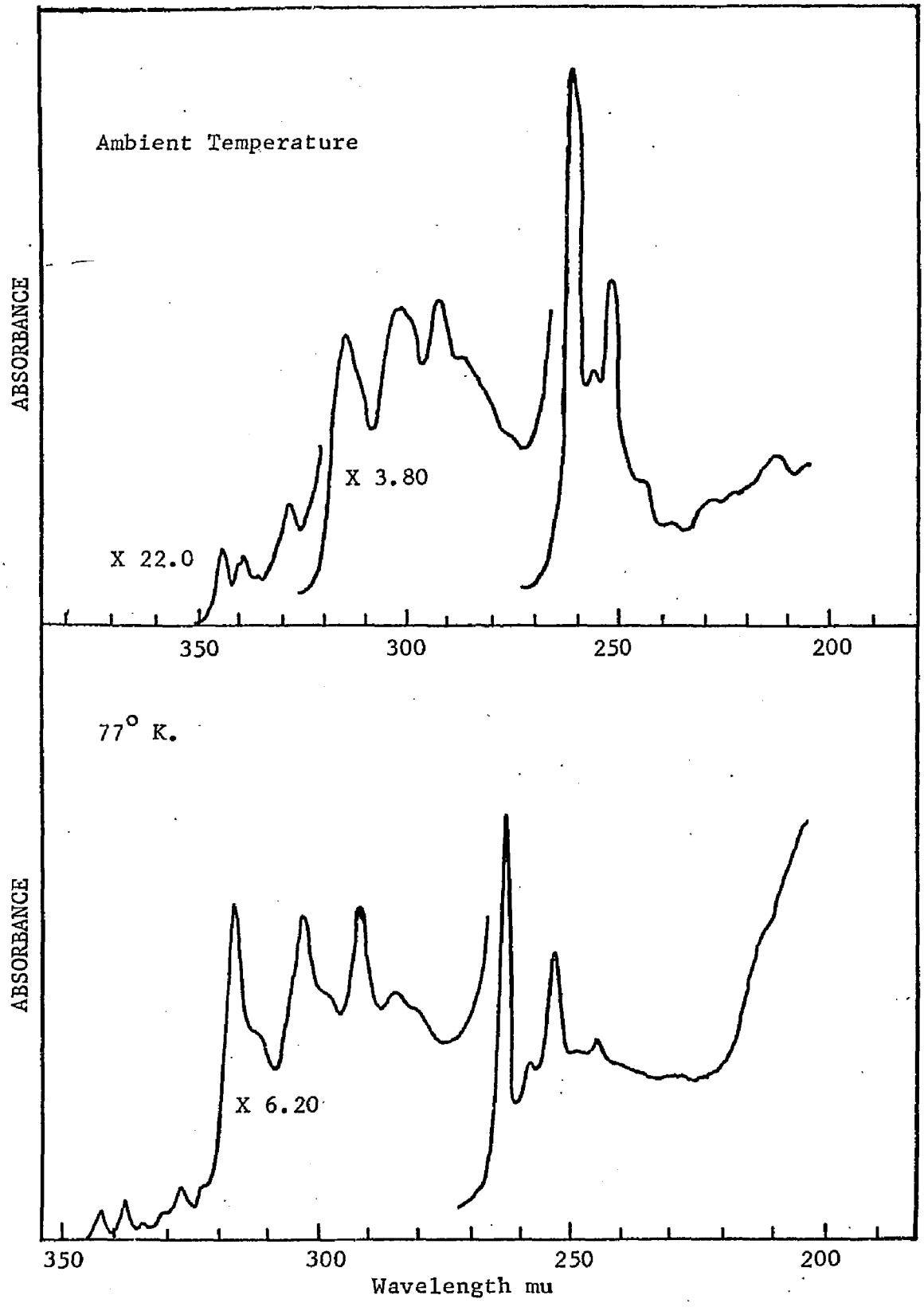

FIGURE 17. Ambient Temperature and 77° K. Absorption of 1,2-Benzfluorene from 3-MP Solution.

TABLE XI

Absorption Frequencies and Extinction Coefficients of 1,2-Benzfluorene

Ambient Temperature from 3-MP Solution

Å	cm^{-1}	$\epsilon(1./m.cm.)\underline{x}10^4$
3445	29,028	0.110
3395	29,455	0.110
3360	29,762	0.068
3280	30,448	0.171
3240	30,864	0.162
3150	31,746	1.19
3025	33,058	1.28
2930	34,130	1.32
2875	34,783	1.10
2620	38,168	8.45
2575	38,835	4.57
2530	39,526	5.28
2485	40,241	2.59
2445	40,900	2.23
2370	42,194	1.82
2130	46,948	2.68
2070	48,309	2.47
2010	49,751	2.56

Table XI (Continued)

77°K From 3-MP Solution		
Å	cm^{-1}	$\Delta\nu$
3435	29,112	0
3395	29,455	343
3355	29,806	694
3315	30,166	1,054
3275	30,534	1,422
3235	30,912	1,800
3185	31,397	0
3115	32,103	706
3050	32,787	1,390
2985	33,501	2,104
2930	34,130	2,733
2870	34,843	3,446
2635	37,951	0
2590	38,610	659
2545	39,293	1,342
2500	40,000	
2460	40,650	

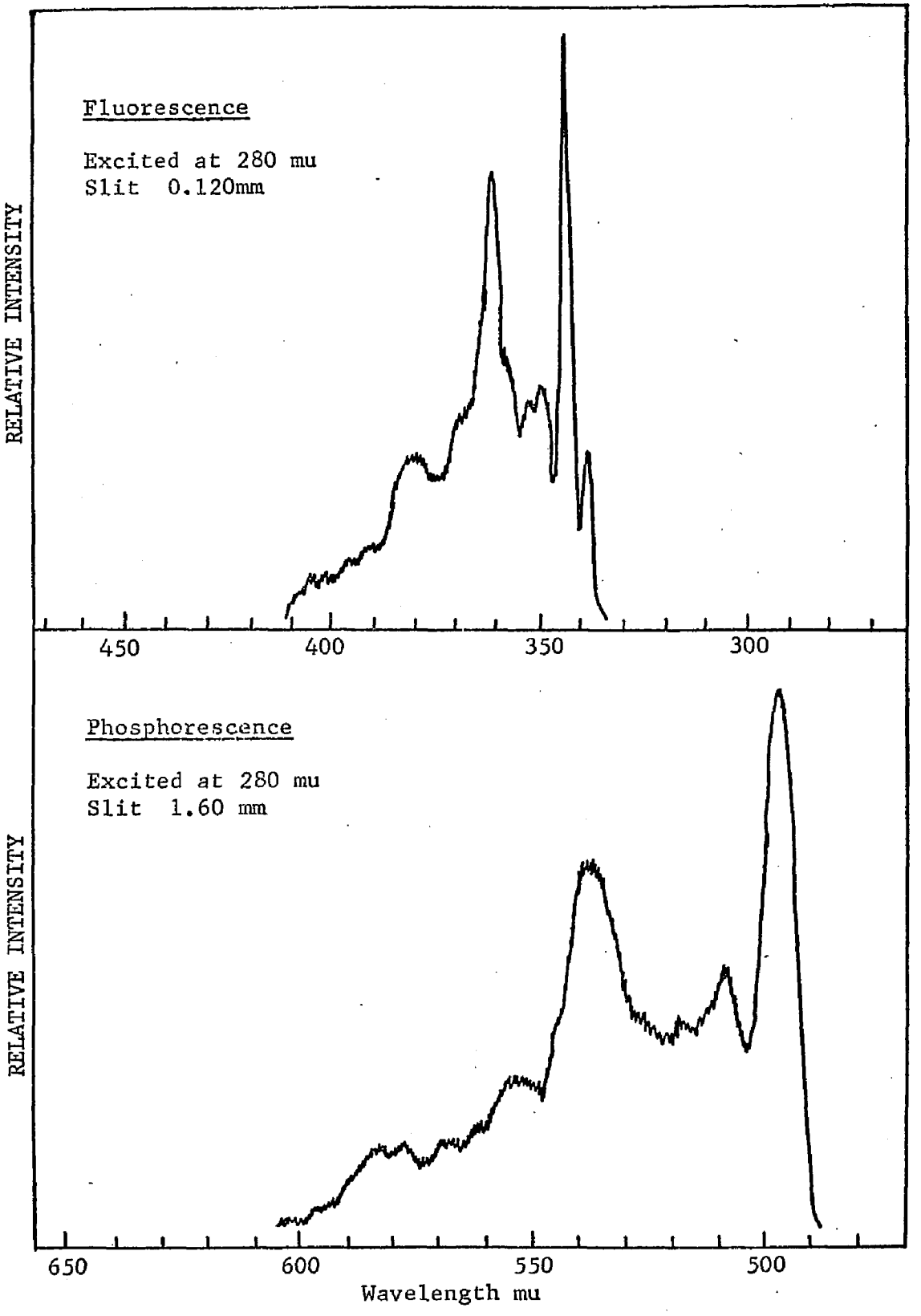

FIGURE 18. Fluorescence and Phosphorescence at 77° K. of 1,2-Benzfluorene from 3-MP Solution.

TABLE XII

Emission Frequencies of 1,2-Benzfluorene

Fluorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3395	29,455	0
3440	29,070	385
3505	28,531	924
3530	28,329	1,126
3575	27,972	1,483
3620	27,624	1,831
3720	26,882	2,573
3820	26,178	3,277
4050	24,691	4,764

Phosphorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
4980	20,080	0
5095	19,627	453
5195	19,249	831
5270	18,975	1,105
5380	18,587	1,493
5550	18,018	2,062
5830	17,153	2,927

of 2-phenylnaphthalene.[44] This compound is also an important member of the series studied in this work. The electronic spectra of 2-phenylnaphthalene have been reproduced from Holloway's work. The absorption spectra of 2-phenylnaphthalene in 3-MP solution at ambient temperature and in IPMP solution at 77°K are shown in Figure 19. The absorption frequencies and extinction coefficients measured for 2-phenylnaphthalene are given in Table XIII. The fluorescence and phosphorescence spectra from 3-MP solutions at 77°K are shown in Figure 20 and the emission frequencies are given in Table XIV.

H. The Spectra of 1,2,7,8-Dibenzfluorene

1,2,7,8-Dibenzfluorene is a close analogue of 1,2-benzfluorene. This dibenzfluorene molecule has C_{2v} symmetry and the interacting subsystems are now identical. This molecule should also be planar since it suffers no internal strains.

The absorption spectra of 1,2,7,8-dibenzfluorene in 3-MP solution at ambient temperature and at 77°K in EPA solution are shown in Figure 21. The absorption frequencies are given in Table XV. The fluorescence and phosphorescence spectra at 77°K from 3-MP solutions are shown in Figure 22,

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[44] H.E. Holloway, ibid.

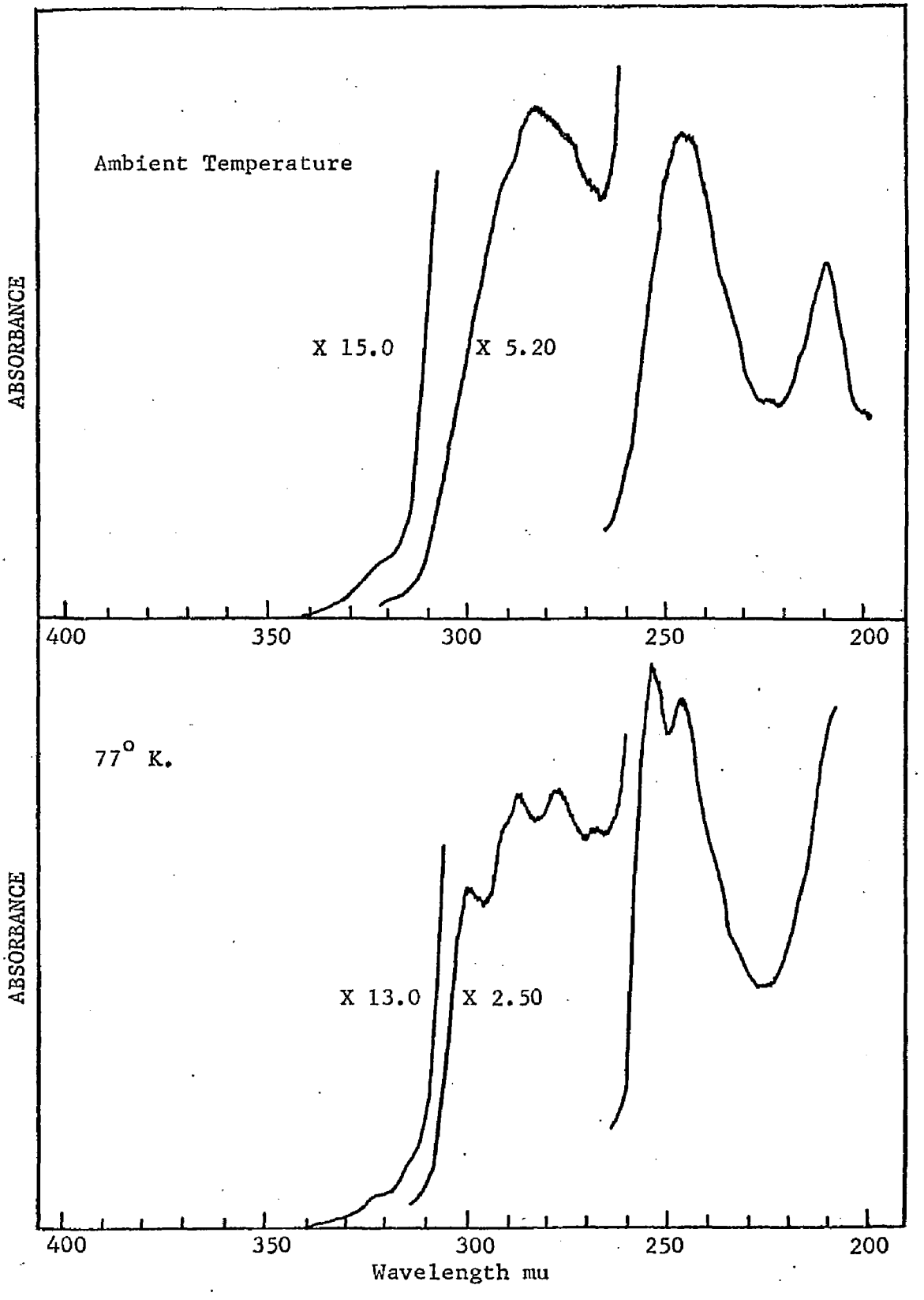


FIGURE 19. Ambient Temperature and 77° K. Absorption of 2-Phenylnaphthalene from 3-MP and IPMP Solutions.

TABLE XIII

Absorption Frequencies and Extinction Coefficients of 2-Phenylnaphthalene

Ambient Temperature from 3-MP Solution

Å	cm^{-1}	$\epsilon(1./m.cm.)\underline{x}10^4$
3225	31,008	
2870	34,843	1.25
2500	40,000	5.67
2120	47,170	4.12

$77^{o}K$ from IPMP Solution

Å	cm^{-1}	$\Delta\nu$
3225	31,008	0
3010	33,222	0
2890	34,602	1,380
2780	35,971	2,749
2680	37,313	4,091
2550	39,215	0
2465	40,568	1,353

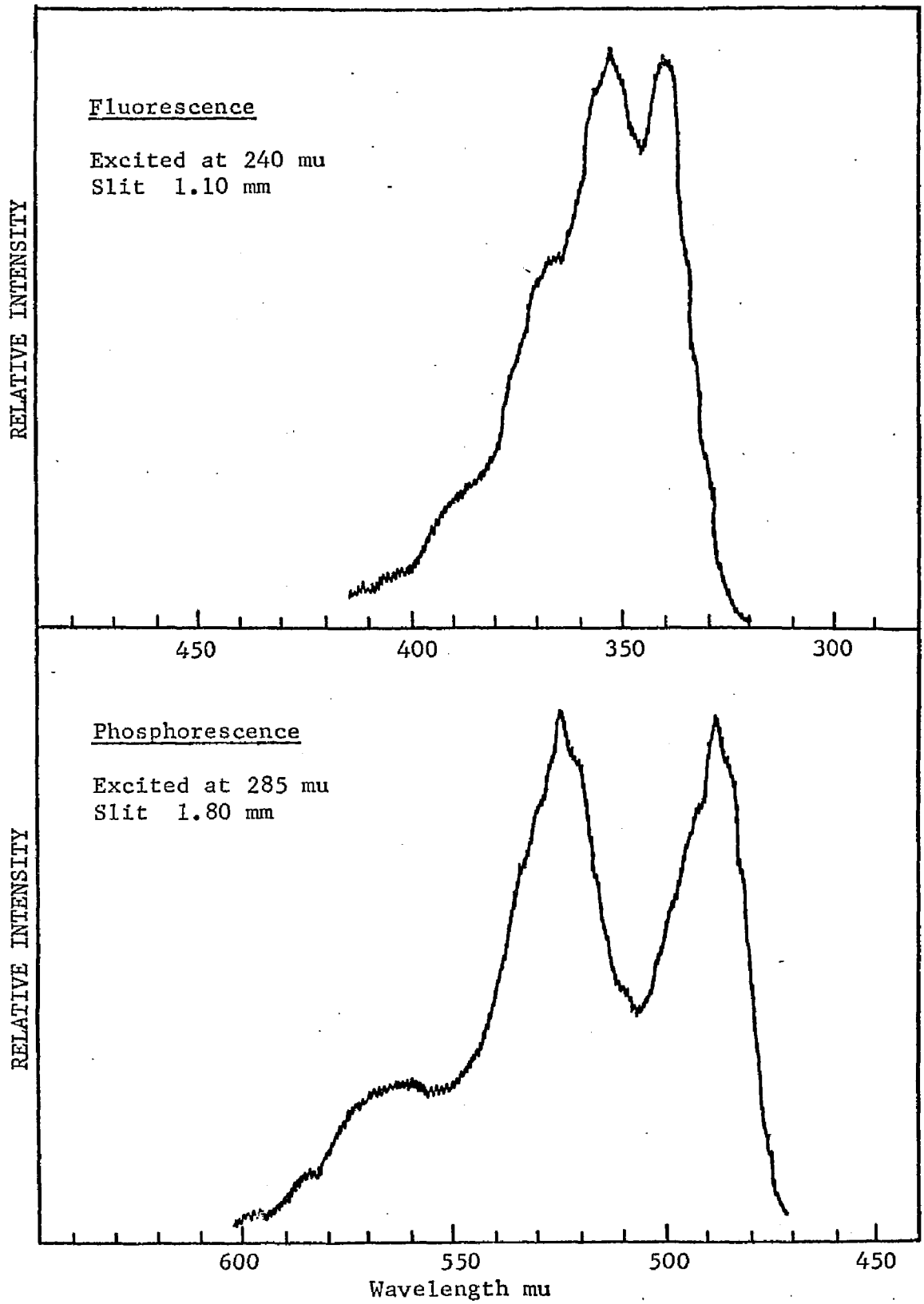


FIGURE 20. Fluorescence and Phosphorescence at 77° K. of 2-Phenylnaphthalene from 3-MP Solution.

TABLE XIV

Emission Frequencies of 2-Phenylnaphthalene

Fluorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3420	29,240	0
3545	28,209	1,031
3680	27,174	2,066
3825	26,144	3,096

Phosphorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
4870	20,534	0
5230	19,120	1,414
5650	17,699	2,835

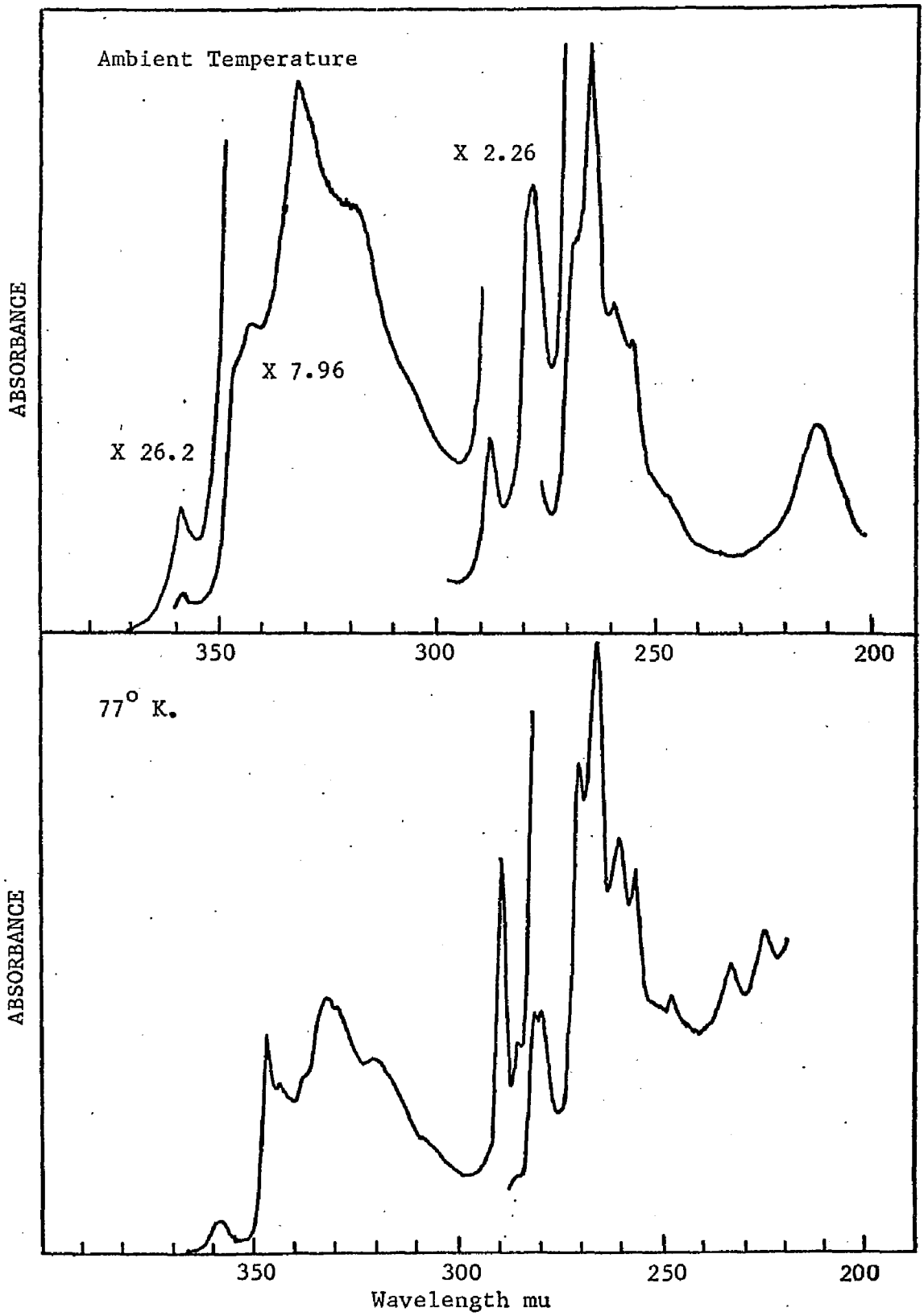


FIGURE 21. Ambient Temperature and 77° K. Absorption of 1,2,7,8-Dibenzfluorene from 3-MP and EPA Solutions.

TABLE XV

Absorption Frequencies of 1,2,7,8-Dibenzfluorene

Ambient Temperature from 3-MP Solution

Å	cm^{-1}
3584	27,902
3457	28,927
3420	29,240
3312	30,193
3200	31,250
3077	32,500
2874	34,795
2780	35,971
2678	37,341
2642	37,850
2592	38,580
2553	39,170
2505	39,920
2466	40,552
2128	46,992

Table XV (Continued)

77°K from EPA Solution

Å	cm^{-1}	$\Delta\nu$
3579	27,941	0
3461	28,893	0
3434	29,120	227
3370	29,674	781
3317	30,148	1,255
3289	30,404	1,511
3200	31,250	2,357
3077	32,500	3,607
2896	34,530	0
2854	35,038	508
2812	35,562	1,032
2795	35,778	1,248
2704	36,982	0
2662	37,556	574
2609	38,329	1,347
2567	38,956	1,974
2478	40,355	
2336	42,808	
2257	44,365	

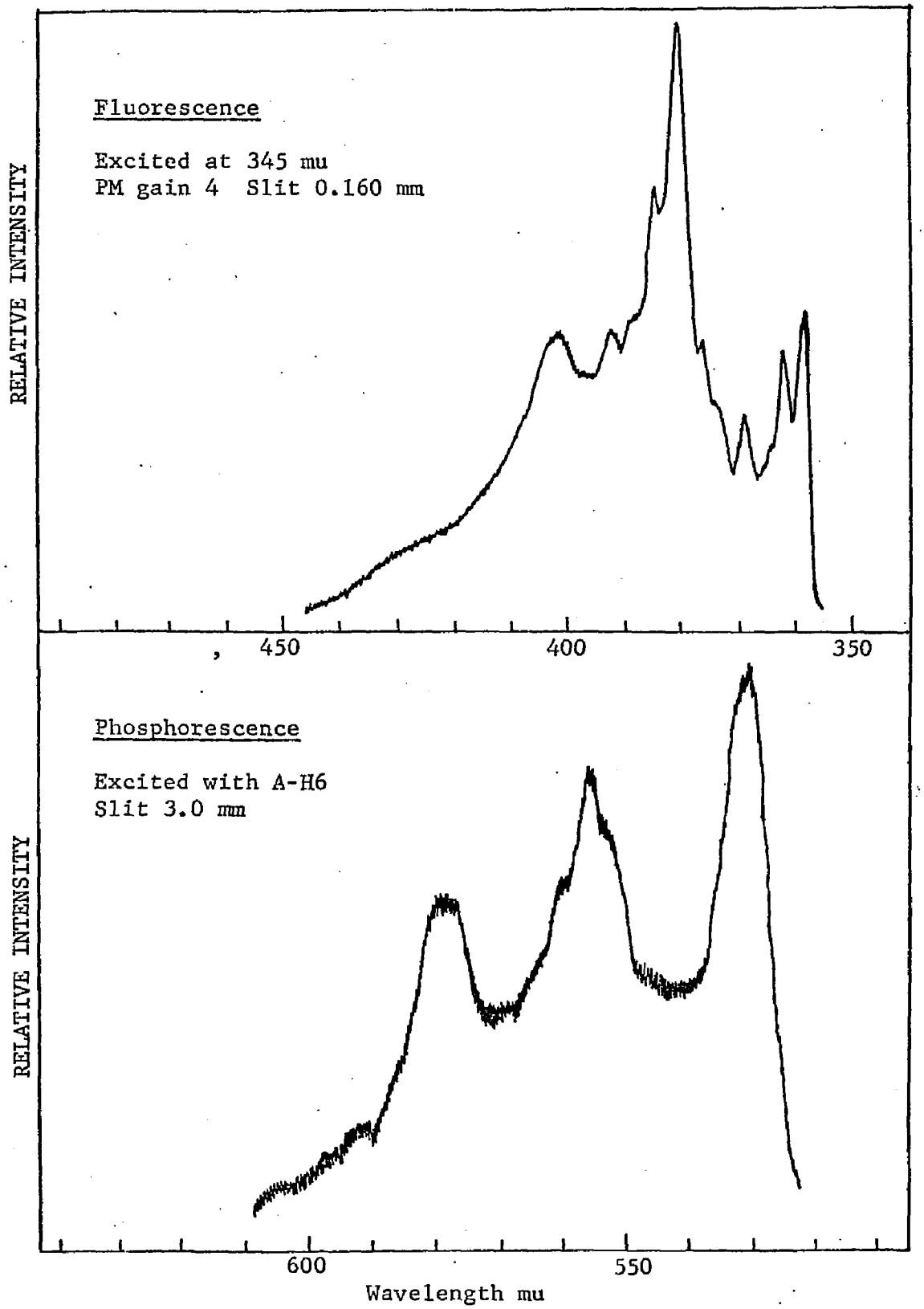


FIGURE 22. Fluorescence and Phosphorescence at 77° K. of 1,2,7,8-Dibenzfluorene from 3-MP Solution.

and the emission frequencies are given in Table XVI.

I. The Spectra of 2,3-Benzbiphenylene

The absorption spectrum of 2,3-benzbiphenylene in 3-MP solution at ambient temperature is shown in Figure 23. In Figure 24 is the ambient temperature absorption spectrum from absolute ethanol solution. The absorption frequencies and extinction coefficients are given in Table XVII. 2,3-Benzbiphenylene is only very slightly soluble in any of the normal glassing solvents and it becomes unusually insoluble as the temperature is lowered. This extremely low solubility at 77°K makes absorption measurements of the long wavelength transition impossible. In Figure 24 are shown a well resolved display of the high energy transitions and a poorly resolved display of the low energy transition of 2,3-benzbiphenylene in 3-MP solution at 77°K. The low temperature absorption frequencies are also shown in Table XVII. The absorption polarization spectrum is also shown in Figure 23. This spectrum was obtained by measuring the polarization of the fluorescence excitation spectrum. The experimental arrangement used to determine the polarizations is shown in Figure 26. Amplifier meter readings were taken and assumed to be directly proportional to the fluorescence intensity.

TABLE XVI

Emission Frequencies of 1,2,7,8-Dibenzfluorene

Fluorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3593	27,832	0
3626	27,580	252
3694	27,071	761
3747	26,688	1,144
3771	26,518	1,314
3814	26,219	1,613
3856	25,934	1,898
3892	25,694	2,138
3932	25,432	2,400
4030	24,814	3,018

Phosphorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
5320	18,800	0
5560	17,990	810
5790	17,270	1,530

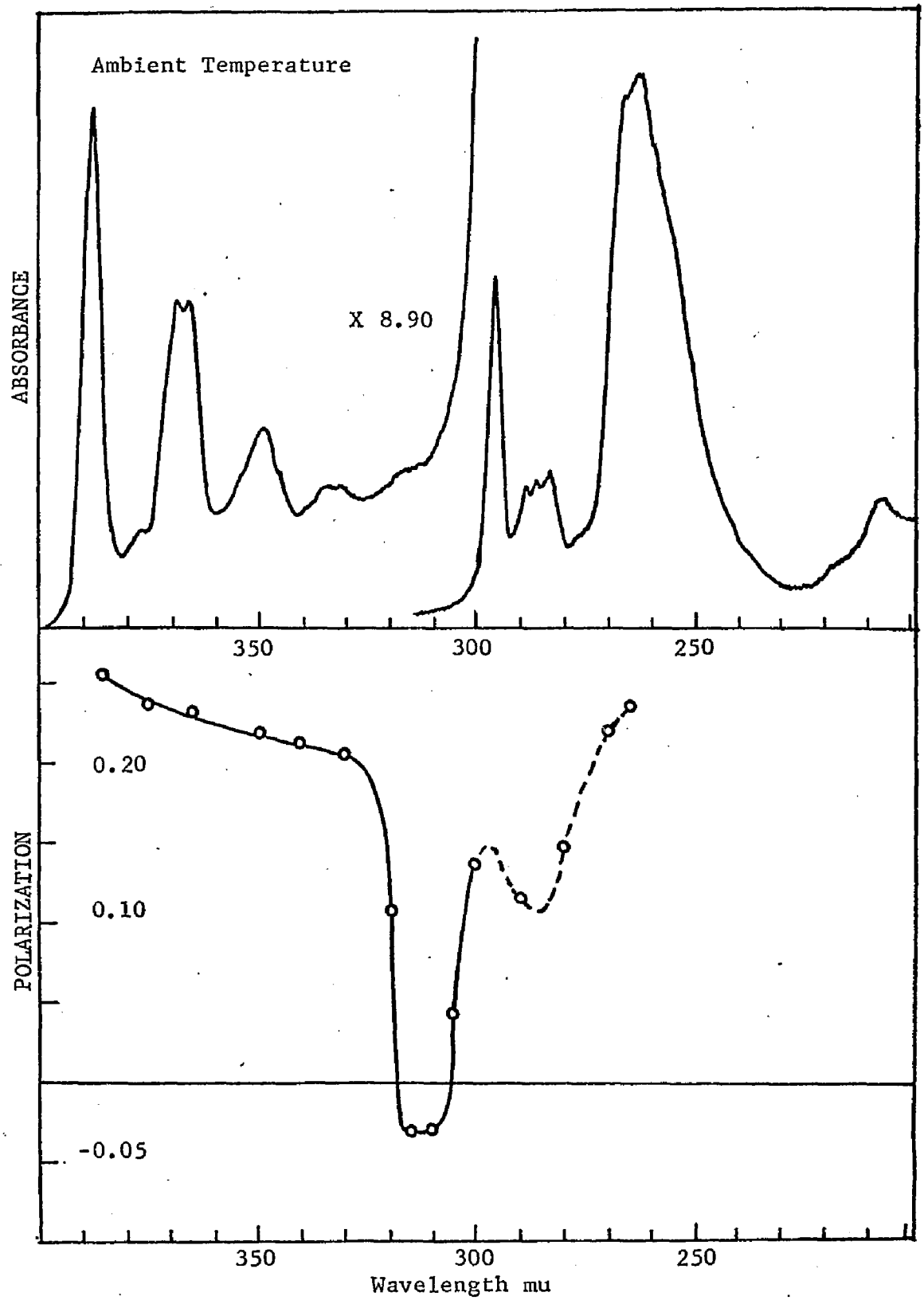


Figure 23. Ambient Temperature Absorption and 77° K. Polarization Spectra of 2,3-Benzbiphenylene from 3-MP Solutions.

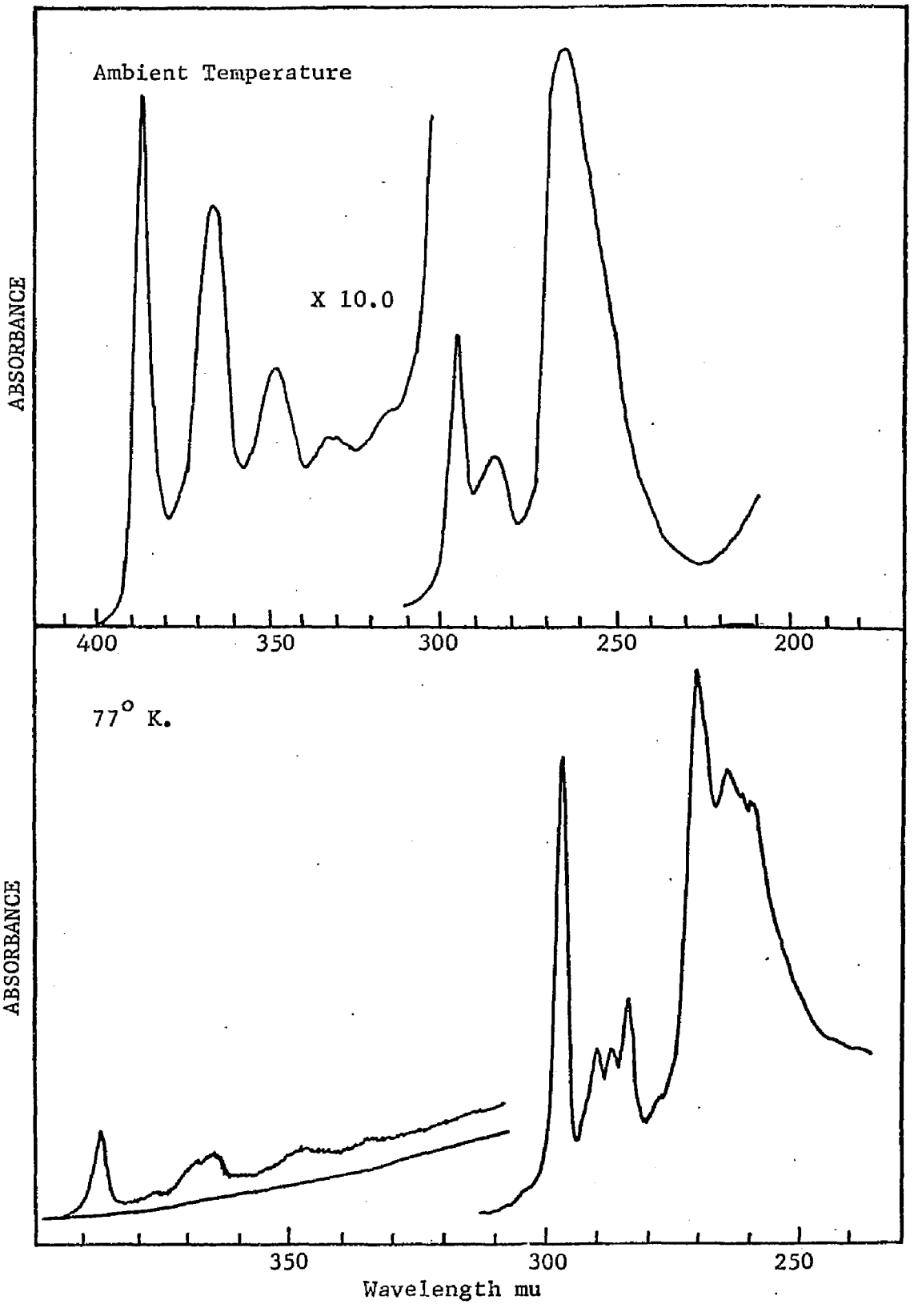


FIGURE 24. Ambient Temperature and 77° K. Absorption of 2,3-Benzbiphenylene from Ethanol and 3-MP Solutions.

TABLE XVII

Absorption Frequencies and Extinction Coefficients of 2,3-Benzbiphenylene

Ambient Temperature from 3-MP Solution

Å	cm^{-1}	$\Delta\nu$
3876	25,800	0
3684	27,144	1,344
3658	27,337	1,537
3553	28,145	2,345
3482	28,719	2,919
3450	28,986	3,186
3337	29,967	4,167
3308	30,230	4,430
2963	33,750	0
2893	34,566	816
2866	34,892	1,142
2835	35,273	1,523
2762	36,206	0
2635	37,951	0

Table XVII (Continued)

Ambient Temperature from Ethanol Solution

Å	cm^{-1}	ϵ(liter/mole cm.)$\times 10^4$
3869	25,846	0.734
3665	27,285	0.525
3483	28,711	0.323
3330	30,030	0.234
3140	31,847	0.272
2959	33,795	3.67
2857	35,000	2.47
2638	37,908	7.78

$77^{\circ}K$ from 3-MP Solution

Å	cm^{-1}	$\Delta\nu$
3870	25,840	0
2971	33,659	0
2906	34,412	753
2878	34,746	1,087
2843	35,174	1,515
2780	35,971	0
2702	37,010	0
2641	37,864	854
2600	38,462	1,452

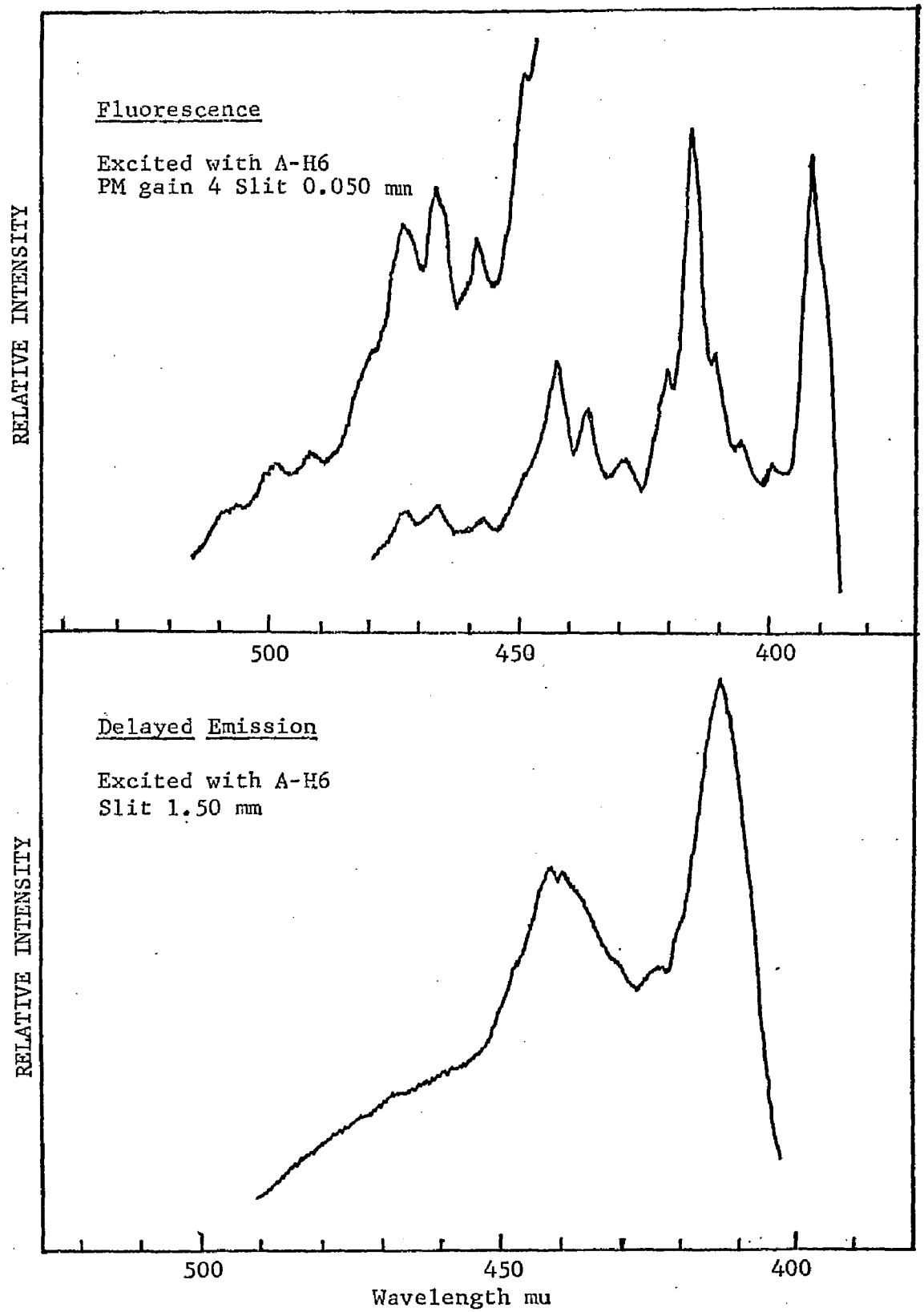


FIGURE 25. Fluorescence and Delayed Emission at 77° K. of 2,3-Benzbiphenylene from 3-MP Solution.

TABLE XVIII

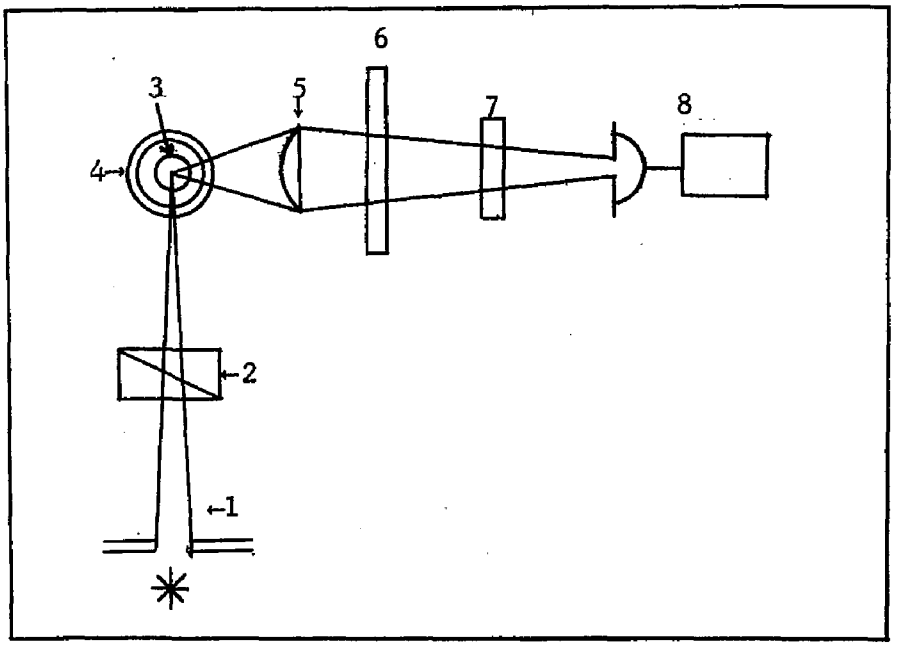
Emission Frequencies of 2,3-Benzbiphenylene

Fluorescence from 3-MP Solution at 77°K

Å	cm^{-1}	$\Delta\nu$
3928	25,458	0
4005	24,969	489
4060	24,630	828
4120	24,272	1,186
4169	23,986	1,472
4205	23,781	1,677
4290	23,310	2,148
4374	22,862	2,596
4443	22,507	2,951
4485	22,297	3,161
4591	21,782	3,676
4673	21,400	4,058
4742	21,088	4,370

FIGURE 26

Polarized Fluorescence Excitation Apparatus



1. Monochromatic exciting light from Cary 15 monochromator.
2. Wolloston prism
   Vertically polarized at all times
3. Sample cell; 20 mm quartz tube
4. Supersil quartz dewar
5. 50 mm cylindrical far u.v. lens
6. 6" x 6" polaroid sheet from Pioneer Scientific Corp.
   161 Great Neck Road, Great Neck, N.Y.
7. Corning glass Filter; CS 3-74
8. 1-P28 photomultiplier tube connected to an Aminco
   Microphotometer Amplifier.

The polarization is given by

$$P = \frac{I_{||} - I_{\perp}}{I_{||} + I_{\perp}}$$

in which $I_{||}$ indicates the light intensity when the polarizing prism and the analyzing polaroid are parallel and $I_{\perp}$ indicates the light intensity when they are crossed. Theoretically the maximum polarization is -1/2 while the minimum value is -1/3.[45,46] In practice these extremes are never realized. It was assumed that the ambient temperature fluorescence was totally depolarized and measurements made on the room temperature emission were used to calibrate the apparatus. It was found that a small constant correction factor of +0.086 had to be applied to polarization measurements at all wavelengths. By not using a second monochromator to monitor the emission it was assumed that the molecular fluorescence does not have mixed polarization. Normally this assumption may be a poor one, but the magnitude of the polarization suggests that the molecular fluorescence has, at most, only slightly mixed polarization. By monitoring the total fluorescence emission one avoids the need for carefully calculating large polarization correction

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[45] A.C. Albrecht, J. Mol. Spec., 6, 84 (1961).

[46] Tohru Azumi and S.P. McGlynn, J. Chem. Phys., 37, 2413 (1962).

factors and is also able to make measurements at much lower emission light intensities.

The molecular fluorescence depicted in Figure 25 is from 3-MP solution at 77°K. Excitation was by the 1,000 watt A-H6 Hg lamp. The exciting light was filtered by a Corning glass filter which passes light between 3050 and 3950Å. Use of the high exciting light intensity allowed the use of very narrow slits (0.05mm) and a photomultiplier gain setting of 4 on the 0-10% slide-wire for the Cary 14. These conditions are ideal for recording high resolution spectra and consequently the highly structured molecular fluorescence is well resolved. A delayed emission was recorded by means of the phosphorescence technique in the same region in which the fluorescence appears. This emission is also depicted in Figure 25 and the frequencies of both emissions are given in Table XIX. The fluorescence emission exhibits a 1,470 cm^{-1} vibrational mode characteristic of an $^1A \leftarrow {}^1L_a$ emission. In addition, superimposed on these major vibrations is another mode which is composed of progressions of about 360-480 cm^{-1}. There is a mismatch of 382 cm^{-1} between the 0-0 bands of absorption and emission. There is only a reasonable mirror image relationship between absorption and emission. It is felt that the fluorescence would compare much

more favorably with a well resolved low temperature absorption spectrum. The intensity of the delayed emission is very low. Its very high energy position makes it extremely unlikely that this emission is the molecular phosphorescence. Solutions of the compound are stable to long periods of illumination with high energy light both at room temperature and at 77°K. Any photochemical reaction which takes place must be a reversable one. The species which gives rise to the delayed emission must ultimately decay to the original molecule. Candidates for this shortlived species are not immediately evident. The emissions of 2,3-benzbiphenylene will be discussed further after the theoretical calculations have been considered.

J. Preliminary Discussion

1. Absorption Spectra

In the compounds benzanthrene, 3,4-benzfluorene, and 3,4,5,6-dibenzfluorene the lowest energy absorptive transition is the $^1A \rightarrow {}^1L_a$. The 0-0 bands for these transitions follow: 3,4,5,6-dibenzfluorene, 27,360 cm^{-1}; benzanthrene, 28,610 cm^{-1}; and 3,4-benzfluorene, 29,735 cm^{-1}. In these molecules the short-axis interaction of the naphthalene portion of the molecule with the rest of the molecule is large enough so that

the naphthalene $^1A \rightarrow {}^1L_a$ transition has been stabilized to the point that this transition is lower in energy than the $^1A \rightarrow {}^1L_b$. In all three cases the naphthalene ring is fused in the 1-position to the rest of the molecule, and the naphthalene ring is nearly coplanar with the remainder of the molecule. The first of these effects, (fusing in the 1-naphthyl position) is not sufficient to lower the energy of the ^1L_a state below that of the ^1L_b. Two similar molecules which are fused in the 1-position but in which the lowest transition is the $^1A \rightarrow {}^1L_b$ are 1-phenylnaphthalene and 1,1-binaphthyl. 1-Phenylnaphthalene has just been discussed. The absorption spectrum of 1,1-binaphthyl is depicted by Jaffé.[47] In 1,1'-binaphthyl the $^1A \rightarrow {}^1L_a$ transition occurs at about 31,250 cm^{-1} or at about 500 cm^{-1} higher energy than the $^1A \rightarrow {}^1L_b$ transition. Obviously then the stabilization of the ^1L_a state is increased over that of the ^1L_b when the subportions of the molecules are near coplanarity. Another molecule which is planar and in which the naphthalene portion of the molecule is fused in the 1-position is fluoranthene. Rather surprisingly in fluoranthene it is apparently the $^1A \rightarrow {}^1L_b$ transition which is lowest in energy.[48] In that case

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[47] Jaffé, op. cit., p.311.

[48] Wharton, op.cit., p.44.

several vibrational bands identified as belonging to the $^1A \rightarrow {}^1L_b$ transition can be seen at the low energy side of the $^1A \rightarrow {}^1L_a$ transition. As well as being planar, or nearly planar, the naphthalene ring is fused to the benzene ring in both short-axis positions. One would certainly expect the ^1L_a state to be the lowest energy excited state. One of two other factors must also be important in the stability of the ^1L_b state. One possibility is that significant interaction takes place through the methylene bridge in the benz- and dibenzfluorenes. However, this factor cannot be extremely important because in both 3,4-benzfluorene and 3,4,5,6-dibenzfluorene the methylene bridge joins the naphthalene ring in the 2-position and should interact to a large extent with the ^1L_a state. The amount of interaction through this bridge can be qualitatively evaluated. In 3,4-benzfluorene the bridge is joined to the naphthalene 2-position and in benzanthrene it is joined to a short-axis naphthalene position. In benzanthrene the $^1A \rightarrow {}^1L_b$ transition is 1,125 cm^{-1} to the red of that in 3,4-benzfluorene. One must be careful not to equate this energy difference to an absolute difference in energy of the two ^1L_a states. The energy of the ground states also determines the transition energies. However,

there is no a priori reason to expect the ground state of 3,4-benzfluorene to be more stable than the ground state in benzanthrene. The other factor which may be important in determining the energy of the $^1A \rightarrow {}^1L_b$ transition in fluoranthene is that fact that fluoranthene is a formally nonalternant molecule. From the classical case of azulene a precedent can be drawn for the stabilization of the ^1L_b state. In nonalternant azulene the $^1A \rightarrow {}^1L_b$ transition has shifted into the visible at 14,350 cm^{-1}.[49] It seems likely that the fluoranthene molecule in some respects is unique and that it cannot be properly considered to be a member of the series of compounds studied in this work. If the methylene carbon in the benz- and dibenzfluorenes participated in the pi-MO electronic distribution to any significant extent these molecules would also have to be considered to be nonalternant. One must conclude, in view of the absorption spectra, that the benz- and dibenzfluorenes show less nonalternant characteristics than does fluoranthene which itself does not show the strong nonalternant effects shown by azulene.

In the compounds 2-phenylnaphthalene, 1,2-benzfluorene, 2,3-benzfluorene, and 1,2,7,8-dibenzfluorene the $^1A \rightarrow {}^1L_b$

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[49] Jaffé, op. cit., 341.

transition is the lowest energy absorptive transition. The 0-0 band energies of the $^1A \rightarrow {}^1L_a$ and the $^1A \rightarrow {}^1L_b$ transitions of several molecules are shown in Table XIX. In 1,2-benzfluorene and 2,3-benzfluorene several vibrational bands of the $^1A \rightarrow {}^1L_b$ transition are visible. As one might expect, the absorption spectra of these molecules are very similar. The $^1A \rightarrow {}^1L_b$ transitions are within 325 cm^{-1} of each other while the $^1A \rightarrow {}^1L_a$ transitions are isoenergetic. The main difference between the two spectra is the absence of a strong well defined transition in the 45,450-50,000 cm^{-1} region of the 1,2-benzfluorene spectrum. In the 1,2,7,8-dibenzfluorene molecule the $^1A \rightarrow {}^1L_b$ transition has shifted only slightly to the red of the corresponding transition in 1,2- and 2,3-benzfluorene ($\sim$1,200 cm^{-1}) while the $^1A \rightarrow {}^1L_a$ transition has shifted very much to the red ($\sim$6,000 cm^{-1}).

The 0-0 band of the $^1A \rightarrow {}^1L_a$ transition in benzanthrene, all the benzfluorenes, and all the dibenzfluorenes with the possible exception of 2,3-benzfluorene show a curious phenomena. As the temperature is lowered to liquid nitrogen temperatures the 0-0 band of the $^1A \rightarrow {}^1L_a$ transition becomes much sharper and more intense in comparison with the rest of the spectrum. The

TABLE XIX

$^1A \rightarrow {}^1L_b$ and $^1A \rightarrow {}^1L_a$ Transition Energies

Molecule	$^1A \rightarrow {}^1L_b$		$^1A \rightarrow {}^1L_a$	
	Å	cm^{-1}	Å	cm^{-1}
1,2,7,8-DBF	3579	27,940	3465	28,860
2,3-BF	3397	29,438	3185	31,397
1,2-BF	3435	29,112	3185	31,397
2-PN	3225	31,008	3010	33,222
1-PN	3192	31,330	2886	34,660
3,4,5,6-DBF	?	?	3655	27,360
Benzanthrene	?	?	3495	28,610
3,4-BF	?	?	3363	29,735

DBF = dibenzfluorene

BF = benzfluorene

PN = phenylnaphthalene

author has also observed the same effect in the spectra of fluorene and fluorenone. This effect is especially prevalent in the benzanthrene and 1,2,7,8-dibenzfluorene molecules Since this effect is observed only in the 0-0 band of the $^1A \rightarrow {}^1L_a$ transition the phenomena can not be attributed to a sharpening of the minimum in the ground state potential well as the temperature is lowered. The only reasonable explanation is that as the temperature is lowered the minimum in the ^1L_a potential well shifts such that at 77^oK the minimum in the well lies nearly directly above the minimum in the ground state potential well. The reason why this phenomenon occurs throughout this series of molecules remains unclear. Further analysis of the absorption spectra will be postponed until theoretical calculations have been considered.

2. Emission Spectra

In the molecules 3,4-benzfluorene, benzanthrene, and 3,4,5,6-dibenzfluorene the lowest singlet absorptive state is the ^1L_a. Consequently the fluorescence spectra of the molecules are typical of those originating from a ^1L_a state. In all three cases the fluorescences exhibit a good mirror image relationship

with the absorptions. The splittings between the 0-0 bands of absorption and emission are small and may be further exaggerated by slight self absorption of the fluorescences. The splittings between major vibrational transitions are about 1400 cm^{-1} which is typical of the naphthalene ring breathing frequency. In addition to the major vibrational modes, each emission exhibits further low energy vibrational splittings. These low energy vibrational splittings have not been assigned.

The $^1A \rightarrow {}^1L_b$ transition is the lowest energy singlet absorptive transition in the molecules 1-phenylnaphthalene, 2-phenylnaphthalene, 1,2-benzfluorene, 2,3-benzfluorene, and 1,2,7,8-benzfluorene. Consequently it is expected that the fluorescences be characteristic of $^1A \leftarrow {}^1L_b$ emissions. The fluorescence in 1-phenylnaphthalene is characterized as an ^1L_b emission and will not be further discussed at this time. The fluorescence of 2-phenylnaphthalene is not easily recognizable as a $^1A \leftarrow {}^1L_b$ emission. The lack of structure is easily attributable to the shallow nature of the ^1L_b potential well, even at 77°K. The vibrational bands which are discernible show splittings of about 1,000 cm^{-1} which is a larger interval than one would expect for a $^1A \leftarrow {}^1L_b$ transition but smaller than that expected for a $^1A \leftarrow {}^1L_a$ transition.[50] There is no doubt

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[50] Jaffé, ibid., p.303.

however that the lowest energy excited state as well as the lowest energy equilibrium excited state is the ^1L_b. In many respects the 2-phenylnaphthalene molecule is dissimilar to the other members of this series of molecules. It shows the closest resemblence to the 1-phenylnaphthalene molecule in that many angles of rotation about the fusing bond are allowed at ambient temperatures. However, 2-phenylnaphthalene fails to show fine structure in either the $^1A \rightarrow {}^1L_b$ or $^1A \leftarrow {}^1L_b$ transitions at 77^oK. This is indicative of a very shallow potential well both in the ground state and in the ^1L_b excited state. This subject will be treated further in the theoretical section.

The fluorescence of 2,3-benzfluorene shown in Figure 16 is a display of an extremely well resolved $^1A \leftarrow {}^1L_b$ emission. The 0-0 band of the fluorescence is at only 26 cm^{-1} lower energy than the 0-0 band in absorption. A single vibrational progression is shown through at least four vibrational bands. The vibrational splittings are measured to be 650-750 cm^{-1}. The small splitting between absorption and emission and the slight anharmonicity of the vibrational progression suggest only a very slight geometry change between the ground state and the ^1L_b excited state.

The fluorescence of 1,2-benzfluorene reveals an

interesting effect. The fluorescence again is typical of a $^1A \leftarrow {}^1L_b$ emission and exhibits the superposition of two vibrational progressions. One is approximately 400 cm^{-1} and the other is approximately 700 cm^{-1}. The interesting effect is that the 0-0 band of the fluorescence is exactly isoenergetic with the second absorption band and not with the lowest energy absorption band. Holloway concluded that the first absorptive band was $1 \rightarrow 0$ vibrational transition, that is, was a hot band. This transition very slightly loses intensity at 77°K but this loss in intensity is hardly enough to warrant assigning the transition to be a hot band. Alternatively, this mismatch between absorption and emission can be considered to be a result of some change in the excited state after absorption and before emission. If an antistokes shift takes place a difference between the geometry of the Franck-Condon and the equilibrium excited states is required. Moreover it is required that the lowest vibrational level in the equilibrium excited state be isoenergetic with the second vibrational level in the Franck-Condon excited state. A complete absence of this effect was just observed in the case of 2,3-benzfluorene. In 1,2-benzfluorene the 0-0 fluorescence band is exactly isoenergetic with the $1 \rightarrow 0$ absorptive transition and the fluorescence fairly well mirror images the first few

bands in the absorption spectrum. The match of the fluorescence 0-0 band with the $0 \rightarrow 1$ absorption band implies little change in geometry between the Franck-Condon and the equilibrium excited states. This type of explanation is hardly one that would be implied in an antistokes shift. Nevertheless the answer to the mismatch must lie in some change in the excited state rather than in postulating populations of vibrationally excited levels in the ground state at $77^{\circ}K$. This is an interesting phenomena and one worthy of further study.

The 0-0 band in the fluorescence of 1,2,7,8-dibenzfluorene lies 110 cm^{-1} lower in energy than the 0-0 band in the absorption. Only one band belonging to the $^1A \rightarrow {}^1L_b$ transition is visible in the absorption. Consequently determination of mirror image symmetry is impossible. The fluorescence shows a considerable amount of fine structure and lies at about 1,600 cm^{-1} lower energy than does the fluorescence of 1,2-benzfluorene. Except for the fact that in 1,2-benzfluorene the $2 \leftarrow 0$ vibrational band is intense, while it is not in 1,2,7,8-dibenzfluorene, the fluorescences of the two compounds are very similar.

The lowest lying triplet state in the molecules 1-phenylnaphthalene, 2-phenylnaphthalene, 3,4-benzfluorene, 3,4,5,6-dibenzfluorene, 1,2-benzfluorene, 2,3-benzfluorene, and 1,2,7,8-dibenzfluorene is the ^3L_a state. In Table XX the energies

TABLE XX

Triplet State Energies

Molecule	Å	cm^{-1}
fluorene	4211	23,750
naphthalene	4695	21,299
1-chloronaphthalene	4762	21,000
1-phenylnaphthalene	4980	20,080
2-phenylnaphthalene	4870	20,534
1,2-benzfluorene	4980	20,080
2,3-benzfluorene	4992	20,032
3,4-benzfluorene	5181	19,301
1,2,7,8-dibenzfluorene	5210	18,800
3,4,5,6-dibenzfluorene	?	?
fluoranthene	5390	18,550
11,12-benzfluoranthene	5480	18,248
benzanthrene	5510	18,149

of the phosphorescence 0-0 bands of these compounds and those of some others are given for comparison.

The phosphorescence of 3,4,5,6-dibenzfluorene shown in Figure 8 is obviously not that of the original molecular species. The high energy portion of the spectrum is likely the emission from photodecomposition products. Such high intensity and high energy exciting light must be used to produce a readable signal that by the time the spectrum can be scanned the decomposition has taken place. What is felt to be part of the molecular phosphorescence can be seen as structure on the low energy side of the emission curve. The remainder of the phosphorescence is postulated in Figure 7 from a consideration of the emissions of the other members of the series. Harris found what he felt to be a molecular emission on the high energy side of the phosphorescence of 3,4-benzfluorene.[51] This author was able to purify away the spurious emission in 3,4-benzfluorene and reproduce it again photochemically at will. However in 3,4,5,6-dibenzfluorene the photodecomposition reaction is so fast that it cannot be followed by available spectral methods. In the cases of benzanthrene, the benzfluorenes and the dibenzfluorenes the phosphorescence quantum yield is

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[51]Harris, op. cit., p.115.

very low. Holloway reports a phosphorescence quantum yield for 1,2-benzfluorene of 0.0045 and this phosphorescence is much easier to monitor than many of the others reported in this work.[52] In most cases the molecular phosphorescences must be excited with the full intensity of the A-H6 lamp. These conditions are so severe that photochemical reactions in even reasonably stable molecules can be expected.

Considering the size and relative orientations of the molecular subsystems the triplet state energies of the compounds in Table XX generally fall in a predictable order and progress in a suprisingly smooth fashion on moving through the table. The triplet state of naphthalene is stabilized by about 300 cm^{-1} by substitution of a chlorine in the 1-position. The 1-phenylnaphthalene triplet state is further stabilized by about 920 cm^{-1} over that of 1-chloronaphthalene. The largest part of this stabilization must come from pi-orbital interaction between rings. Even in the triplet state, the 1-phenylnaphthalene molecule must be severely twisted out of plane. When the phenyl ring is brought into the naphthalene plane as in 3,4-benzfluorene the triplet state is further stabilized over that of 1-phenyl-naphthalene by 780 cm^{-1}. In 3,4-benzfluorene an additional

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[52] Holloway, op. cit., p.140.

effect, namely that of interaction through the methylene bridge, takes place. A qualitative estimate of the interaction energy through the methylene bridge can be made by consideration of 2-phenylnaphthalene and 2,3-benzfluorene. The 2-phenylnaphthalene triplet state is considered to be planar as the triplet state of 2,3-benzfluorene must be. The triplet state of 2,3-benzfluorene lies at about 500 cm^{-1} lower energy than does that of 2-phenylnaphthalene. One must recognize that these interaction in 2,3-benzfluorene and 2-phenylnaphthalene are essentially long-axis with the naphthalene ring whereas the ^3L_a state is short-axis polarized. Nevertheless this stabilization of 500 cm^{-1} over that of 2-phenylnaphthalene due to the methylene bridge is a major portion of the 780 cm^{-1} stabilization of 3,4-benzfluorene over 1-phenylnaphthalene. In a similar manner the stabilization of the triplet state of 1,2,7,8-dibenzfluorene over that of 1,2-benzfluorene of 1,120 cm^{-1} may be rationalized. For the sake of comparison it can be noted from Table XX that the triplet state of fluoranthene is more stable than that of 3,4-benzfluorene by 750 cm^{-1} and that the triplet state of 11,12-benzfluoranthrene is more stable than that of fluoranthene by about 300 cm^{-1} The obvious misfit in the group is benzanthrene which has a triplet state energy 400 cm^{-1} lower than fluoranthene and even about

100 cm^{-1} lower than the triplet state of 11,12-benzfluoranthene.

3. The Photochemistry of Benzanthrene

Obviously the methylene bridge in benzanthrene must be more important than it is in the benz- and dibenzfluorenes. It was noted earlier that the acidities of the hydrogens on the bridging carbons would be important to the electronic states of these molecules. Streitwieser has made an extensive study of the acidities of hydrogens on bridging carbons in the molecular ground states.[53,54,55,56] Streitwieser's pK values for several hydrocarbons in their electronic ground states are given in Table XXI.

TABLE XXI

pK Values for Several Bridged Hydrocarbons

Compound	pK
Fluorene	22.83
9-Phenylfluorene	18,49
Indene	20.24
4,5-Methylenephenanthrene	22.60
1,2-Benzfluorene	19.97
2,3-Benzfluorene	23.16
3,4-Benzfluorene	19.38
Benzanthrene	20.67

[53] A. Streitwieser, Jr. and W.M. Padgett, II, J. Am. Chem. Soc., 68, 2919 (1964).

[54] A. Streitwieser, Jr., J.I. Brauman, J.H. Hammons, and A.H. Pudjaatmaka, J. Am. Chem. Soc., 87, 386 (1965).

[55] A. Streitwieser, Jr., J.H. Hammons, E. Ciuffaria, and J.I. Brauman, J. Am. Chem. Soc., 89, 59 (1967).

[56] A. Streitwieser, Jr., Alan P. Marchand, A.H. Pudjaatmaka, J. Am. Chem. Soc., 89, 692 (1967).

The acidity of the methylene hydrogens in benzanthrene is within the range of the benzfluorenes. This suggests that the methylene hydrogens of benzanthrene are in approximately the same electronic environment as are those of the benzfluorenes in their electronic ground states. The $^1A \rightarrow {}^1L_a$ transition energy for benzanthrene is 28,610 cm^{-1} or about 1,125 cm^{-1} less than that of 3,4-benzfluorene. The $^1A \leftarrow {}^3L_a$ transition energy for benzanthrene is 18,149 cm^{-1} or about 1,150 cm^{-1} lower than that of 3,4-benzfluorene. The fluorescence and phosphorescence spectra of benzanthrene and 3,4-benzfluorene bear striking resemblance to each other. The vibrational splittings as well as the Franck-Condon contour of the emissions are almost identical. Their only dissimilarity is the difference in their energetic positions. It was estimated from considerations involving 2-phenylnaphthalene and 2,3-benzfluorene that the stabilization of the ^1L_a state by the methylene bridge was 400-500 cm^{-1}. This stabilization is not nearly enough to account for the difference in spectra of the two molecules.

A study was made of the instability of the benzanthrene molecule. A review of this study is in order. The preparation and purification of benzanthrene has been given in a previous section. It was observed that the white plates of the pure

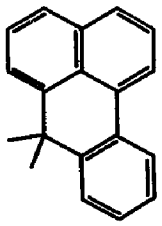
compound began to show visible decomposition after standing a day or two in a bottle under nitrogen. The decomposition left the plates with a yellow color. The compound was stored in a pyrex dessicator under vacuum, but the decomposition was only slightly slower at reduced pressures. The pure white compound could be separated from the yellow decomposition products by chromatography on a very slightly activated alumina column; CCl_4 was used as an elution agent. The pure hydrocarbon was eluted almost immediately and was followed by yellow products. When the pure hydrocarbon was stored in the dark under nitrogen in the freezing compartment of a refrigerator, the decomposition process was retarded to a large extent. A study was made to follow the decomposition process photochemically. The following observations were made.

In glassed hydrocarbon solutions at $77^{\circ}K$ benzanthrene appeared to be stable for several hours to bombardment with the full intensity of the A-H6 lamp, while in hydrocarbon solutions at about 5×10^{-4} M at room temperature, visible decomposition started immediately. The solution turned yellow and a tarry product began to precipitate. Within ten minutes the reaction appeared to be complete. Attempts were made to characterize

the precipitate. No distinct melting point could be observed; there was only a gradual softening process. The precipitate was extracted with hydrocarbon. The ultraviolet absorption spectrum showed that benzanthrene was not present and there were no bands characteristic of a significant concentration of anything. The precipitate was extracted with absolute ethanol and enough product was taken up to give the solution a light yellow color. The ultraviolet absorption spectrum was poorly resolved and there was considerable scattering, but bands were discernible at 2100, 2500 and 2560Å. A less intense band was centered at about 3000Å and the scatter continued well into the visible region. These bands cannot be fitted to the spectra of 1-phenylnaphthalene, 2-phenylnaphthalene, fluoranthene, benzanthrone, or any of the benzfluorenes. In Figure 27 are shown all of the probable decomposition products which involve a transfer of a hydrogen from the methylene bridge to another molecular position. Compounds II through VII are the various H-benz[de]anthracenes. Compound I is aromatic only in so far as the benzene ring contributes aromatic character. The remainder of the molecule is conjugated but nonaromatic. With the exception of 7H-benz[de]-anthracene, none of the ultraviolet spectra of the compounds in Figure 27 have been published in the literature. This makes

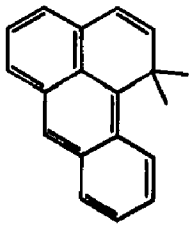
FIGURE 27

Possible Benzanthrene Photochemical Products



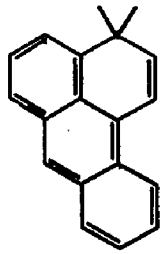
I

7H-benz[de]anthracene



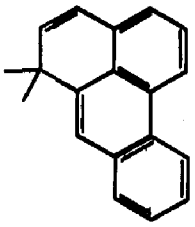
II

1H-benz[de]anthracene



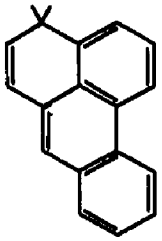
III

3H-benz[de]anthracene



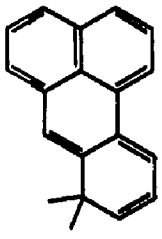
IV

6H-benz[de]anthracene



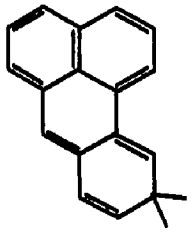
V

4H-benz[de]anthracene



VI

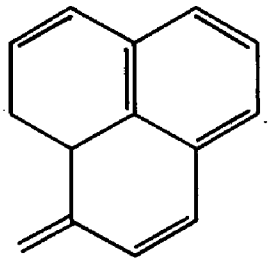
8H-benz[de]anthracene



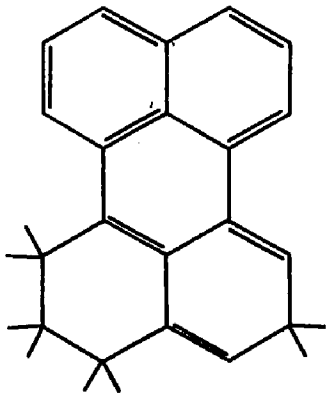
VII

10H-benz[de]anthracene

identification of the photodecomposition product by means of absorption spectra more difficult. However compounds II and III may be considered to be stubstituted anthracenes and their spectra should be much like those of 1- and 9- substituted anthracenes. In like manner compounds IV and V may be considered to be substituted phenanthrenes. Compounds VI and VII present more of a problem. They can be considered to be derivatives of an aromatic substituted 1-phenylene (1-benzonaphthene).

i.e. 

or as a tetrahydroperylene.

i.e. 

(1,2,3,5-tetrahydroperylene see 10H-benz[de]anthracene)

Unfortunately, neither the spectra of the appropriately substituted phenylenes nor those of the hydroperylenes are available. The observed bands do not fit the transitions in phenanthrene or substituted phenanthrenes. The bands at 2100, 2500, and 2560Å match reasonably well the $^1A \rightarrow {}^1B_b$ and $^1A \rightarrow {}^1C_b$ transitions in the spectra of 9-substituted anthracenes. The weaker band at 3000Å does not fit any transition in anthracene and its origin must be from an additional species. On this evidence one of the major photochemical rearrangement products is assigned to be either molecule II, 1H-benz[de]anthracene or molecule III, 3H-benz[de]anthracene, although molecules VI and VII cannot be ruled out.

The first step in the photochemical process corresponds to an abstraction of hydrogen from the methylene bridge. It is believed that this process does not take place in the excited singlet state. The fluorescence is almost a perfect mirror image of the absorption and the 0-0 band shift between absorption and emission is very small. It will be recalled that the phosphorescence was characterized to be that of a compound in which more extensive conjugation was in effect than that of the original hydrocarbon. Obviously the first step in the photochemical decomposition must be a reversible one since no net

effect could be found after extended radiation of glassy solutions. As a second step a rather extensive hydrogen migration and attack back on the ring is indicated. Local thawing upon excitation, the range of migration and the ethanol solution absorption spectrum indicate that either II or III are reasonable choices for the site of hydrogen migration. For II to be formed a hydrogen intramolecular migration of about four and one-half Å is required; while for III a migration of about five and one-half Å is required. No experiment was carried out which would distinguish between structures II and III. The third step in the overall process is a rapid photoinduced polymerization of the hydrocarbon produced in step two. It will be noted that the styrene-type linkages on either II or III should be readily amenable to polymerization. Because of the very small quantities of benzanthrene available and a lack of interest in the photochemical polymerization no further studies of this process were carried out.

After the extended discussion of the benzanthrene molecule and its photochemistry the next logical step is to postulate that the triplet state of benzanthrene is dissociative and that its phosphorescence is characteristic of a benzanthrene

anion or radical. Fortunately the absorption spectra of the anions of benzanthrene and the benzfluorenes have been studied.[57] In Appendix B the absorption spectra of several Li salts of the benzfluorenes and benzanthrene in cyclohexylamine and ether solutions have been reproduced. The lithium salt of benzanthrenyl anion in cyclohexylamine solution has a transition at 4440Å with an extinction coefficient of 34,600 l./mole cm. and a lower energy transition between 5000Å and 7000Å which exhibits several vibrational maxiam. The lowest energy vibrational band which may be the 0-0 band is at 6400Å and has an extinction coefficient of 6,700 l./mole cm. The salt in ether solution shows similar transitions which are blue shifted about 850 cm^{-1}. Even allowing for further blue shift of the lowest energy transition when the anion is in nonpolar solvent and is associated with a hydrogen ion rather than a lithium cation, it is likely that the lowest energy absorptive transition will still be at lower energy than the phosphorescence observed for benzanthrene, which has a 0-0 band at 5510Å. This leaves little choice other than the conclusion that the phosphorescence observed for benzanthrene is not characteristic of the benzanthrenyl anion. A priori little can be predicted about the emissions from the

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[57] A. Streitwieser, Jr. and J.I. Brauman, J. Am. Chem. Soc., 85, 2633 (1963).

dissociative benzanthrene radical; however, as a general rule the singlet absorptive transitions for radical species are observed to have only slightly different energies from those of the corresponding anions. The last observation alone should be sufficient to rule out the observed phosphorescence as characteristic of the radical dissociative state of benzanthrene. Hence it must be concluded that the benzanthrene absorption, fluorescence, and phosphorescence spectra are all characteristic of the benzanthrene molecule. This requires that the photochemical reactions be separate and processes competing with those of the emissions and, in addition, leaves the red shifts of the benzanthrene spectra over those of 3,4-benzfluorene unrationalized. It is the opinion of this author that these spectral shifts cannot be rationalized by comparison of benzanthrene spectra with those of 1-phenylnaphthalene, 2-phenylnaphthalene and the benzfluorenes. It is concluded that the energies of the excited states relative to the ground state in the benzanthrene molecule are characteristic only of the benzanthrene molecule. Resemblance of the spectra of benzanthrene to those of the benzfluorenes is a result of the shapes of the potential wells in the ground and excited states and the potential well shapes are a function of molecular geometry which of necessity is much the same in benzanthrene as it is in 3,4-benzfluorene.

CHAPTER IV

THEORETICAL RESULTS AND CONCLUSIONS

A. 1-Phenylnaphthalene at 90^{o}

The electronic energy states of 1-phenylnaphthalene were calculated as a function of the angle θ between rings that is illustrated in Figure 28.

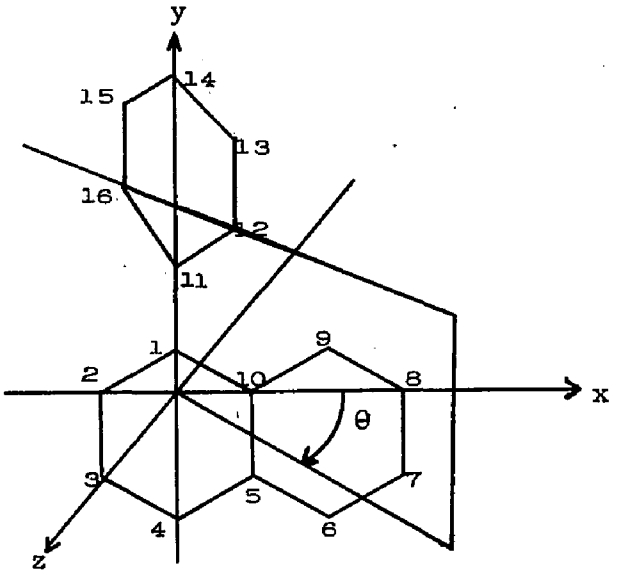

FIGURE 28. The 1-Phenylnaphthalene Molecule

The calculation was made for angles θ = 90^{o}, 55^{o}, 45^{o} and 0^{0}. The angle θ = 0^{0} corresponds to the completely planar molecule, while 90^{o} corresponds to the orientation in which the rings are orthogonal to each other.

The 90° calculation will be considered first. With the rings in this configuration the pi-orbital interaction between rings would be expected to be at an absolute minimum. The value for $\beta_{1\text{-}11} \cos\theta$ is, of course, zero in this configuration. One would expect that the calculated MO's would be recognizable as those of benzene and naphthalene. Indeed, the MO's listed in Table XXII in order of increasing energy are easily recognizable to be essentially either those of benzene or naphthalene after the SCF calculation. These conclusions can be drawn by picking off the AO coefficients for a given MO given in the table of final eigenvectos. See eq. (1). One would expect several different types of transitions to be possible for this given set of MO's. Transitions such as $\psi_7 \rightarrow \psi_8$ are almost pure naphthalene in origin while one such as the $\psi_5 \rightarrow \psi_{11}$ transition is a nearly pure benzene transition. As well as these transitions, transitions which will be referred to as charge transfer, CT, transitions for the $\theta = 90^{\circ}$ calculation (i.e., the $\psi_8 \rightarrow \psi_{11}$ transition) are possible. In Table XXIII the predicted values for transition energies, oscillator strengths, transition moments, transition polarizations and dipole moments are given for the singlet transitions.

TABLE XXII

MO Symmetries and Identities from the 90° SCF-MO Calculation

MO	Orbital*	Identification
ψ_{13}	$B_{1u}N$	Naphthalene
ψ_{12}	$E_{2u}B$	Benzene
ψ_{11}	$E_{2u}B$	Benzene
ψ_{10}	$B_{3g}N$	Naphthalene
ψ_9	$\sim B_{2g}N$	Naphthalene
ψ_8	$\sim A_{u}N$	Naphthalene
ψ_7	$B_{1u}N$	Naphthalene
ψ_6	$E_{1g}B$	Benzene
ψ_5	$E_{1g}B$	Benzene
ψ_4	$B_{3g}N$	Naphthalene
ψ_3	$B_{2g}N$	Naphthalene
ψ_2	$A_{2u}B$	Benzene
ψ_1	$B_{1u}N$	Naphthalene

* In addition to the normal symmetry notation a B or an N has been added to identify to which half of the molecule the MO belongs.

TABLE XXIII

1-Phenylnaphthalene, 90°, Singlet Transitions

Transition		Energy ev	Energy cm^{-1}	Å	F	M	Trans. Pol.	D.M.
ψ_8^9	$^1L_{aN}$	4.4824	30,155	2766	0.325	0.910	y	0.133
ψ_8^{10}	$^1L_{bN}$	4.2605	34,365	2910	-----	-----	y	0.007
ψ_8^{11}	CT	5.9047	47,649	2099	-----	-----	z	21.22
ψ_8^{12}	CT	5.7700	46,541	2149	-----	-----	mixed	21.14
ψ_8^{13}	F_N	5.8681	47,332	2113	-----	-----	mixed	0.000
ψ_7^9	$^1B_{bN}$	5.8136	46,892	2133	2.071	2.017	~x	0.052
ψ_7^{10}	$^1B_{aN}$	6.4355	51,909	1926	0.914	1.274	y	0.093
ψ_6^9	CT	5.9074	47,649	2099	-----	-----	~z	21.74
ψ_6^{10}	CT	7.0188	56,614	1767	-----	-----	~z	21.46
ψ_6^{11}	$^1L_{aB}$	6.1590	49,678	2013	0.059	0.332	mixed	0.121
ψ_6^{12}	$^1B_{bB}$	7.0177	56,605	1767	1.200	1.397	z	0.000
ψ_5^9	CT	5.7700	46,541	2149	-----	-----	mixed	21.84
ψ_5^{11}	$^1L_{bB}$	4.9065	39,576	2527	-----	-----	mixed	0.000
ψ_4^9	$^1C_{bN}$	6.2782	50,640	1975	0.059	0.329	~y	0.058
ψ_4^{10}	$?_N$	6.2022	50,027	1999	-----	-----	~y	0.007
ψ_7^{11}	CT	7.0188	56,614	1767	-----	-----	~z	21.46
ψ_7^{12}	CT	6.9230	55,841	1791	-----	-----	mixed	21.46

The naphthalene and benzene transitions compare favorably with similar ones done on the separate systems by Pople[58] and Pariser.[59] These comparisons are made in Table XXIV. The comparisons of these results with naphthalene transitions are excellent and the present values fall between those of Pople and Pariser. In the case of benzene the comparisons are not strictly valid because the A_{2uB} MO of benzene was not included in the configuration interaction scheme. Although the transition symmetries of the benzene transitions are correct and the labeling of the $^1A \rightarrow {}^1B_{bB}$ and the $^1A \rightarrow {}^1B_{aB}$ transitions is probably correct, the energies are likely to be slightly high because the A_{2uB} MO was not included in the CI calculation. Nevertheless these benzene transitions fall at only slightly higher energies than do those of Pariser and Pople. It is interesting to note that the remaining degeneracy in the benzene system has been partially removed. Pariser and Pople report, as a necessary result, the degeneracy of the ^1B_b and ^1B_a states. In the present calculation this degeneracy has been very slightly removed. After configuration interaction,

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[58] J.A. Pople, Proc. Phys. Soc., 68, 81 (1955).

[59] R. Pariser, loc. cit.

TABLE XXIV

Benzene and Naphthalene Transition Energies

Benzene Transitions

Transition	Energy cm^{-1}	Oscillator Strength	Contributor
$^1A \rightarrow {}^1L_{bB}$	38,000		a
	39,500	0.000	b
	37,900	0.000	c
	39,580	0.000	d
$^1A \rightarrow {}^1L_{aB}$	48,000		a
	43,000	-----	b
	48,070	0.000	c
	49,680	0.059	d
$^1A \rightarrow {}^1B_{bB}$	54,500		a
$^1A \rightarrow {}^1B_{aB}$	56,000	-----	b
	52,820	2.215	c
	56,890	0.966	d
	56,600	1.200	

Table XXIV (Continued)

Transition	Energy cm^{-1}	Oscillator Strength	Contributor
$^1A \rightarrow {}^1L_{bN}$	32,000		a
	35,500	-----	b
	32,410	0.000	c
	34,365	0.000	d
$^1A \rightarrow {}^1L_{aN}$	34,500		a
	37,500	-----	b
	32,410	0.265	c
	36,155	0.325	d
$^1A \rightarrow {}^1B_{bN}$	45,500		a
	49,500	-----	b
	47,900	2.115	c
	46,890	2.071	d
$^1A \rightarrow {}^1B_{aN}$	60,000		a
	50,000	-----	b
	57,230	0.000	c
	51,909	0.414	d

Contributors:

a. experimental values
b. Pople Reference 15
c. Pariser Reference 3
d. This work

including the naphthalene localized MO's, the splitting is about 0.025ev between the ^1B_a and ^1B_b states. If one follows the benzene MO's as the angle between rings changes it can be seen, as expected because of greater CI between subsystems, that the $^1B_{bB}$-$^1B_{aB}$ split becomes larger.

Transitions which are the result of excitations involving both benzene and naphthalene MO's merit some consideration. These transitions, as a result of the molecular configuration, must be forbidden and show zero oscillator strengths. In this calculation these excited states all show very high dipole moments; 21.1-218D. If one places full positive and negative charges at the centers of the phenyl and naphthyl rings and considers the charge separation, the resulting calculated dipole moment is 21.5D. This phenomena is a result of the highly localized character of the unoccupied as well as the occupied MO's. If one takes into account the fact that the two ring systems need not meet requirements for stability of a ground state complex because of the σ-bond between rings, these transitions meet the requirements of classical intramolecular charge transfer transitions outlined by Mulliken.[60]

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[60] R.S. Mulliken, J. Am. Chem. Soc., 74, 811 (1952).

As long as the pi-orbital interaction between rings remains nearly zero, the MO's remain essentially localized, and considering these transitions to be charge transfer transitions should be valid. Some of the lower energy CT transitions are tabulated in Table XXV.

TABLE XXV

Charge Transfer Transitions in 90° 1-Phenylnaphthalene

Transition	Energy cm^{-1}	CT direction
ψ_5^9	46,540	
ψ_5^{10}	55,910	benzene to naphthalene
ψ_6^9	47,650	
ψ_6^{10}	56,614	
ψ_8^{12}	46,540	
ψ_8^{11}	47,650	naphthalene to benzene
ψ_7^{12}	55,840	
ψ_7^{11}	56,614	

Two observations can be made from Table XXV. First, charge transfer transitions occur both from benzene to naphthalene

and from naphthalene to benzene. Second, the CT transitions for this molecular configuration occur in degenerate pairs, the next to highest energy pair being not quite degenerate. The reason that these degeneracies remain after configuration interaction is not clear.

A summary of the SCF-MO-CI calculation for the 90^{o} configuration follows:

1. The occupied and unoccupied molecular orbitals are highly localized and characteristic of the benzene and naphthalene portions of the molecule;

2. Electronic transitions are predicted which are characteristic either of pure benzene or of pure naphthalene and these calculated transition energies compare favorably both with those of other similar calculations and with experimental evaluations;

3. New sets of degenerate transitions were predicted to have zero oscillator strengths and high dipole moments and were satisfactorily characterized to be charge transfer transitions for this molecule.

B. 1-Phenylnaphthalene at Intermediate Angles

The results of the calculations for $\theta = 55^{o}$, 45^{o} and 0^{o} will be considered at the same time rather than separately.

In Tables XXVI, XXVII and XXVIII the values for oscillator strengths, transition moments, transition polarizations and dipole moments are given. In Table XXIX the bond orders for all bonds in the ground state and in the $^1L_{aN}$, $^1L_{bN}$, and $^1B_{bN}$ excited states are given for the case of the 55° conformation. These values are considered to be typical of the bond orders in these calculations. In Figure 29 a schematic representation of the lower energy singlet electronic transitions as a function of ring angle is given.

The values of the AO coefficients, C_{ip}, from equation 21 give an insight into the electronic distribution for a given MO. Indeed, for any particular MO equation 21 is applicable.

$$\sum_p C_{ip}^2 = 1 \qquad \ldots.21$$

Since the basis set of AO's remains constant throughout the calculation, C_{ip}^2 should be a measure of the relative electron density at carbon p for MO i. In considering the electronic transitions, one would like to know as much as possible about the molecular orbitals involved. It was observed in the 90° calculation that these MO's were highly localized on either

TABLE XXVI

1-Phenylnaphthalene, 55°, Singlet Transitions

Transition		Energy ev	Energy cm^{-1}	Å	F	M	Trans. Pol.	D.M.
ψ_8^9	$^1L_{aN}$	4.3045	34,720	2880	0.471	1.118	y	0.436
ψ_8^{10}	$^1L_{bN}$	4.2264	34,090	2933	-----	-----	mixed	1.982
ψ_8^{11}	^1M_a	5.3893	43,470	2300	0.228	0.694	mixed	0.118
ψ_8^{12}	?	4.7711	38,484	2598	-----	-----	mixed	7.819
ψ_8^{13}	F_N	6.2734	50,601	1976	0.049	0.299	~y	0.133
ψ_7^9	$^1B_{bN}$	5.7508	46,386	2156	1.360	1.644	~x	0.766
ψ_7^{10}	$^1B_{aN}$	6.5891	53,148	1882	0.118	0.451	y	0.618
ψ_7^{11}	?	6.0259	48,605	2057	------	------	~x	1.907
ψ_6^9	?	5.4580	44,024	2271	-----	-----	~x	5.085
ψ_6^{12}	$^1B_{bB}$	6.0576	48,861	2047	-----	-----	mixed	4.565
ψ_5^9	^1M_b	5.8447	47,143	2121	0.428	0.914	~x	0.435
ψ_4^9	$^1C_{bN}$	6.1389	49,516	2020	-----	-----	~x	0.452

TABLE XXVII

1-Phenylnaphthalene, 45°, Singlet Transitions

Transition		Energy						
		ev	cm^{-1}	Å	F	M	Trans. Pol.	D.M.
ψ_8^9	$^1L_{aN}$	4.2069	33,933	2947	0.546	1.218	~y	0.586
ψ_8^{10}	$^1L_{bN}$	4.2061	33,926	2948	-----	-----	mixed	2.730
ψ_8^{11}	^1M_a	5.2880	42,653	2344	0.208	0.670	mixed	0.452
ψ_8^{12}	?	4.7050	37,950	2635	-----	-----	~y	9.333
ψ_8^{13}	F_N	6.2780	50,638	1975	0.048	0.296	~y	0.407
ψ_7^9	$^1B_{bN}$	5.6976	45,957	2176	1.075	1.468	~x	1.093
ψ_7^{10}	$^1B_{aN}$	6.3915	51,554	1940	0.631	1.062	~y	0.443
ψ_7^{11}	?	5.9844	48,270	2072	-----	-----	~y	4.907
ψ_6^9	?	5.3573	43,212	2314	-----	-----	mixed	5.212
ψ_6^{12}	$^1B_{bB}$	6.1302	49,446	2022	-----	-----	mixed	4.935
ψ_5^9	^1M_b	5.8155	46,908	2132	0.667	1.145	~x	0.337
ψ_4^9	$^1C_{bN}$	6.1706	49,772	2009	-----	-----	~y	2.459

TABLE XXVIII

1-Phenylnaphthalene, 0^{o}, Singlet Transitions

Transition		Energy						
		ev	cm^{-1}	Å	F	M	Trans. Pol.	D.M.
ψ_8^9	$^1L_{aN}$	4.0097	32,342	3092	0.686	1.398	~y	0.704
ψ_8^{10}	$^1L_{bN}$	4.1588	33,545	2981	-----	-----	mixed	3.793
ψ_8^{11}	?	5.1816	41,795	2393	-----	-----	mixed	4.527
ψ_8^{12}	?	4.5766	36,915	2709	-----	-----	mixed	10.18
ψ_8^{13}	F_N	6.2859	50,702	1972	0.050	0.300	y	0.871
ψ_7^9	$^1B_{bN}$	5.5730	44,952	2224	0.553	1.065	~x	1.910
ψ_7^{10}	$^1B_{aN}$	6.3690	51,372	1946	0.583	1.023	~z	0.950
ψ_7^{11}	?	5.8866	47,481	2106	-----	-----	~y	5.593
ψ_6^9	^1M_a	5.1311	41,387	2416	0.161	0.599	mixed	1.480
ψ_6^{12}	$^1B_{bB}$	6.2798	50,653	1974	-----	-----	~y	3.906
ψ_5^9	^1M_b	5.7562	46,430	2154	1.083	1.466	~x	1.161
ψ_4^9	$^1C_{bN}$	6.2112	50,100	1996	-----	-----	~y	2.042

TABLE XXIX

Bond Orders for 55° 1-Phenylnaphthalene

Bond	States			
	S_o	$^1L_a(N)$	$^1L_b(N)$	$^1B_b(N)$
1-2	.729	.508	.615	.614
2-3	.589	.709	.499	.533
3-4	.739	.542	.638	.637
4-5	.538	.532	.536	.536
5-10	.543	.530	.316	.400
5-6	.540	.543	.544	.542
6-7	.740	.563	.648	.645
7-8	.588	.690	.488	.522
8-9	.739	.553	.644	.642
9-10	.543	.561	.552	.550
1-10	.530	.508	.521	.520
1-11	.177	.289	.235	.236
11-12	.656	.617	.633	.628
12-13	.669	.683	.677	.639
13-14	.665	.646	.653	.650
14-15	.665	.646	.653	.647
15-16	.669	.683	.677	.637
11-16	.666	.617	.663	.630

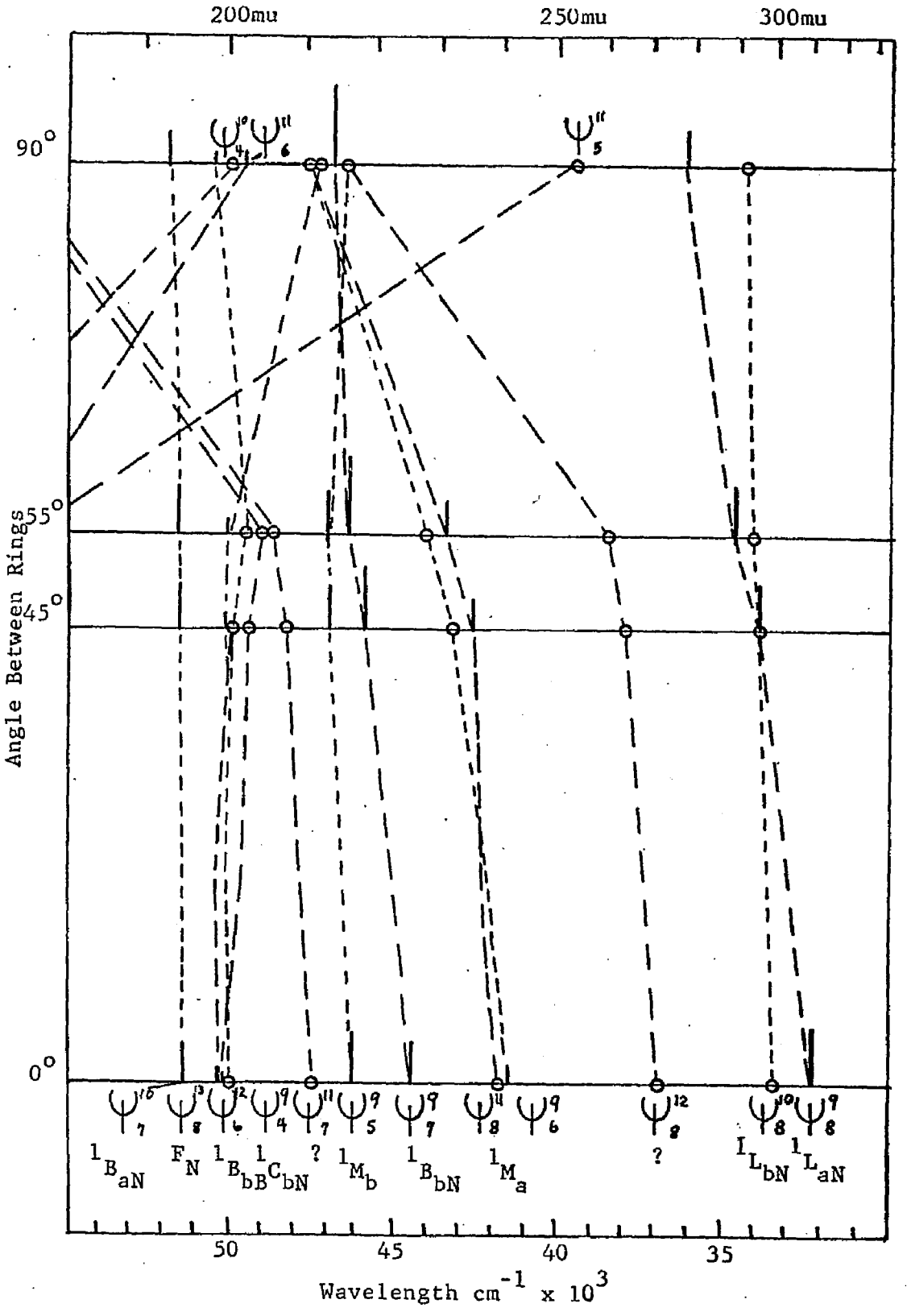

Figure 29. The 1-Phenylnaphthalene Singlet Transitions

benzene or naphthalene. A semi-quantitative evaluation of the delocalization in any given MO would be a valuable quantity. For this purpose a new quantity will be defined in equation 22.

$$I_D = \frac{100 \sum_{11}^{16} C_{ip}^2}{\sum_{11}^{16} C_{ip}^2 + \sum_{1}^{10} C_{ip}^2} = 100 \sum_{11}^{16} C_{ip}^2 \qquad \ldots\ldots 22$$

I_D is a measure of the % benzene character of a given MO. If I_D = 100% the MO will be considered to be localized entirely on the benzene ring while a value of I_D = 0% corresponds to an MO entirely localized on the naphthalene ring. Values between these two extremes indicate the extent of delocalization of the MO. In Table XXX, I_D values from the SCF calculation are listed as a function of ring angle. The data in Table XXX indicate that at 0° some SCF-MO's are almost completely delocalized over both rings (i.e., ψ_6 and ψ_{11} both belonging to benzene at 90°) while other retain almost entirely their submolecule identities (i.e., ψ_5 and ψ_{12} belonging to benzene and ψ_7 and ψ_{10} belonging to naphthalene). Configuration interaction produces sets of configurational states from which the electronic transitions of the molecule are calculated. It is worth noting

TABLE XXX

Extent of Orbital Delocalization, I_D

SCF-MO	90^o	55^o	45^o	0^o
1	0	5.39	8.65	16.1
2	100	91.5	86.4	75.2
3	0	3.33	5.42	10.8
4	0	9.79	15.8	22.3
5	100	99.7	99.5	98.3
6	100	79.1	70.3	55.6
7	0	.02	.04	1.45
8	0	9.09	13.2	20.1
9	0	9.09	13.2	20.1
10	0	.02	.04	1.45
11	100	79.1	70.3	55.6
12	100	99.8	99.5	98.2
13	0	9.42	15.7	22.3

that these states are not consistent from one transition to another. It is apparent that a new set of configurational states is computed for each different electronic distribution.

Some general comments are relevant at this time. The transitions in the 90° configuration, which were characteristic of benzene and agreed well with pure benzene transitions, because of orbital delocalization and configuration interaction shift strongly to the blue as the phenyl ring is rotated from 90°. The $^1A \rightarrow {}^1L_{aB}$ and $^1A \rightarrow {}^1L_{bB}$ transitions lose their identity completely. The $^1A \rightarrow {}^1B_{bB}$ transition is the only benzene transition predicted to remain in the experimentally accessible ultraviolet, and it is calculated to have a very low oscillator strength when the phenyl ring is rotated from 90°. These predictions cause severe doubt that the 1-phenylnaphthalene spectrum can be calculated by the addition of the separate spectra of benzene and naphthalene in the manner done by Jones.[61] The naphthalene transitions, $^1A \rightarrow ({}^1L_{bN}, {}^1L_{aN}, {}^1B_{bN}, {}^1C_{bN}, {}^1B_{aN})$, survive CI and retain a typically naphthalene appearance regardless of the angle of the phenyl ring. Energetically, as one would predict from Table XXX the $^1A \rightarrow {}^1B_{bN}$ transition is

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[61] R.N. Jones, Chem. Rev., 32, 1 (1943).

almost exactly independent of ring angle. Similarly the $^1A \rightarrow {}^1B_{bN}$ and the $^1A \rightarrow {}^1L_{bN}$ transitions vary only slightly with ring angle. The $^1A \rightarrow {}^1L_{aN}$ transition, because of a more significant delocalization of the orbitals involved, shifts red by 0.47ev between the 90^o and the 0^o molecular configurations.

One of the more interesting aspects of this calculation was that of watching the fate of the CT transitions, listed in Table XXV, as the phenyl ring was rotated from 90^o. Before these transitions are discussed a difficulty in interpretation, or perhaps only in nomenclature, must be reviewed and reconsidered. Often in the literature doubtful transitions are said to have CT character or it is said that a particular $\pi \rightarrow \pi^*$ transition is stealing intensity or borrowing intensity from a CT state. In many cases the meaning of these concepts is obscure at best. In this calculation there is a fuzzy interval during which the phenyl ring begins to rotate from 90^o when it is truly doubtful what kind of terminology should be applied to the transitions listed in Table XXV. It seems reasonable that for a transition to be called a CT transition it must involve a significant transfer of electronic charge between the ground state and the excited state in question. When

the molecule in its ground state has a zero dipole moment this requires that the excited state have a significant dipole moment. In the 90^{o} 1-phenylnaphthalene calculation there are four CT transitions, occurring in degenerate pairs, which are in an experimentally interesting region. By the time the molecule is rotated to 55^{o} the degeneracy of these transitions is permanently lost. At angles of less than or equal to 55^{o} two of these transitions are completely forbidden while the other two have significant oscillator strengths. The forbidden transitions retain high dipole moments but are experimentally uninteresting and will be henceforth ignored. The other two transitions which show significant oscillator strengths have in all cases low dipole moments (0.12 - 1.48D as compared with the $^{1}A \rightarrow {}^{1}B_{bN}$ moment which is 1.91D). In the 55^{o}, 45^{o}, and 0^{o} molecular configurations the author considers these to be $\pi \rightarrow \pi^{*}$ transitions typical of the 1-phenylnaphthalene chromophore. For the sake of brevity and in the spirit of the Platt nomenclature the lower energy of these states will be denoted as the $^{1}M_{a}$ state and the higher energy one as the $^{1}M_{b}$ state. The $^{1}A \rightarrow {}^{1}M_{a}$ transitions occurs at 3,000 - 3,600 cm^{-1} lower energy than the $^{1}A \rightarrow {}^{1}B_{bN}$ transition and has an oscillator strength of 0.16 - 0.23.

The $^1A \rightarrow {}^1M_b$ transition occurs at 750 - 1500 cm^{-1} higher energy than the $^1A \rightarrow {}^1B_{bN}$. Its oscillator strength steadily increases from 0.43 to 1.08 as the rings come into plane. In the 0^o configuration the $^1A \rightarrow {}^1M_b$ transition has a higher oscillator strength than the $^1A \rightarrow {}^1B_{bN}$ transition which steadily becomes weaker as the rings come into plane.

A full SCF-MO with CI calculation was also done on the triplet states of 1-phenylnaphthalene in the same molecular configurations that were used in the calculation of the singlets. In Table XXXI the singlet - triplet transition energies are listed for the four lowest energy transitions. In all configurations the lowest lying triplet state is predicted to be the $^3L_{aN}$ state. Although little is experimentally known about the nature of higher triplet states in aromatic hydrocarbons, this leveling of triplet states is not one that would be intuitively predicted by the author. The P.P.P. type of calculation typically does a poorer job on triplet calculations than it does for the singlet manifold. However, it would be out of line to scoff at the results until definitive experimental evidence is available about the energetic levels, vibrational patterns and, in the case of triplet-triplet transitions, to their extinction coefficients in similar compounds. In the 55^o molecular configuration

TABLE XXXI

1-Phenylnaphthalene Singlet-Triplet Transitions

Configuration	Transition	Energy ev	Energy cm^{-1}	Energy Å
90°	$S_o \rightarrow {}^3L_{aN}$	2.117	17,080	5856
	$S_o \rightarrow {}^3L_{bB}$	3.110	25,080	3987
	* $S_o \rightarrow {}^3F_N$	3.361	27,110	3689
	$S_o \rightarrow {}^3L_{bN}$	3.758	30,310	3299
55°	$S_o \rightarrow {}^3L_{aN}$	2.096	16,900	5915
	$S_o \rightarrow {}^3B_{bB}$	3.074	24,800	4032
	* $S_o \rightarrow {}^3F_N$	3.384	27,300	3664
	$S_o \rightarrow {}^3L_{bN}$	3.728	30,070	3326
45°	$S_o \rightarrow {}^3L_{aN}$	2.073	16,720	5982
	$S_o \rightarrow {}^3B_{bB}$	3.037	24,450	4082
	$S_o \rightarrow {}^3M_a$	3.419	27,570	3627
	$S_o \rightarrow {}^3L_{bN}$	3.709	29,920	3342
0°	$S_o \rightarrow {}^3L_{aN}$	1.995	16,090	6016
	$S_o \rightarrow {}^3M_a$	2.961	23,890	4186
	$S_o \rightarrow {}^3B_{bB}$	3.500	28,230	3542
	$S_o \rightarrow {}^3L_{bN}$	3,665	29,560	3383

* The $S_o \rightarrow {}^3F_N$ transition corresponds to a transition in the singlet manifold which is totally forbidden in the 90° configuration and partially forbidden in the other configurations. After the SCF calculation, this transition was characterized as taking place between ψ_8 and ψ_{13}. In the singlet manifold the transition occurs at about 50,000 cm^{-1}.

the following triplet-triplet transitions are predicted to occur:

$$T_1 \rightarrow T_2,\ {}^3L_{aN} \rightarrow {}^3B_{bB} \text{ at } 7{,}893 \text{ cm}^{-1}$$
$$T_1 \rightarrow T_3,\ {}^3L_{aN} \rightarrow {}^3F_{N} \text{ at } 10{,}392 \text{ cm}^{-1}$$

while for the 0^o configuration, there would occur

$$T_1 \rightarrow T_2,\ {}^3L_{aN} \rightarrow {}^3M_{a} \text{ at } 7{,}798 \text{ cm}^{-1}$$
$$T_1 \rightarrow T_3,\ {}^3L_{aN} \rightarrow {}^3B_{bB} \text{ at } 12{,}145 \text{ cm}^{-1}.$$

C. Intramolecular Hydrogen Interactions in the Ground and Excited States

The SCF-MO-CI calculations that were applied to 1-phenylnaphthalene have one distinct disadvantage. The calculation completely ignores all energetic contributions made by the interaction of hydrogen atoms on the rings. Transition energies were predicted on the basis of pi-MO's and carbon skeletal geometries. As the angle between rings becomes smaller two pairs of hydrogens the 9-16 and 2-12, begin to interact strongly. If one is concerned with the actual molecular geometry, and the molecular energy levels as a function of geometry some account must be taken of these interactions. For this reason, in addition to the SCF-MO calculation, the energy of interaction

of these hydrogen pairs was evaluated. Fortunately this type of interaction has been extensively studied.[62,63,64,65,66,67,68] The Buckingham (exp-6) type of potential has long been recognized to be suitable for this type of interaction. This potential has the form given by equation 23a. The constants are empirically

$$U(r) = -a/r^6 + be^{-cr} \qquad \ldots.23a$$

evaluated, usually by fitting vibrational absorption bands. Several different sets of values have been proposed for these constants. Two of these sets were investigated for this problem. The potential expression used by Bartell has the following values for the empirical constants:

$$a = 3.573 \qquad b = 10.51 \qquad c = 2.16$$

These values were obtained by fitting the two limiting cases of long range and short range interactions. The Bartell potential is an example of what is referred to as a soft potential. That is, the exponential term does not become dominant until the

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[63] K.S. Pitzer and E. Catalano, J. Am. Chem. Soc., 78, 4844 (1956).

[64] L.S. Bartell and R.A. Bonham, J. Chem. Phys., 32, 824 (1960).

[65] J. deBoer, Physica, 9, 363 (1942).

[66] L.S. Bartell, J. Chem. Phys., 32, 827 (1960).

[67] Alex Müller, Proc. Roy. Soc., A154, 624 (1936).

[68] Alex Müller, Proc. Roy. Soc., A178, 227 (1941).

interacting species are relatively close together. An example of a harder potential is the Müller potential. In this potential the constants have values given by:

$$a = 4.496 \qquad b = 100.9 \qquad c = 2.645$$

In both cases the constants are evaluated for use in equation 22, in which r is given in atomic units. In this potential the exponential term becomes dominant at slightly longer distances and the interaction potential rises more sharply in the case of the close interactions. It would be hard to pick the best potential for application to this problem intuitively, although it could be reasoned that due to sp^2 bonding, the phenyl and naphthyl hydrogens are held rather rigidly and are less likely to change bond angles or bond distances than they would be if they were tied up in sp^3 bonding. This type of reasoning would lead one to favor the harder potential. The fact is, no matter what the reasoning, that the Müller potential fits the experimental data slightly better than does the Bartell potential. This was considered to be sufficient reason for the adoption of the Müller potential. It is given in its complete form in equation 23b

$$U(r) = -4.496/r^6 + 100.9\ e^{-2.645r} \qquad \ldots.23b$$

The variable r is the hydrogen-hydrogen distance in atomic units. Potential energy diagrams were constructed for the ground state, and the $^1L_{bN}$ and $^1L_{aN}$ excited states and are shown in Figure 30. These diagrams were constructed by the addition of three terms. The first two of these are the U(r) contributions calculated from equation 22 for the 9-16 and 2-12 hydrogen repulsions. The third is the π-molecular energy calculated by the SCF-MO procedure. In the case of the ground state the energy is simply the sum of the one electron ψ_i energy eigenvalues for the filled MO's, at a given θ, taking into account that it is a sixteen electron problem. In the case of the excited states the transition energies from the CI calculation are added to the θ-dependent ground state energies. In the ground state 1-phenylnaphthalene is predicted to have a minimum energy at $\theta = 52.1 \pm 0.3^\circ$, while the $^1L_{bN}$ minimum occurs at $51.2 \pm 0.3^\circ$ and the $^1L_{aN}$ minimum occurs at $48.8 \pm 0.2^\circ$. The $^1L_{bN}$ and the $^1L_{aN}$ potentials cross at 45° because the transitions are predicted in the CI calculation to be isoenergetic at that angle. The ground state potential well is shallower than the $^1L_{bN}$ and $^1L_{aN}$ wells. The barrier to rotation past 90° for the ground state is predicted to be 0.158ev (3.64 kcal/mole), while

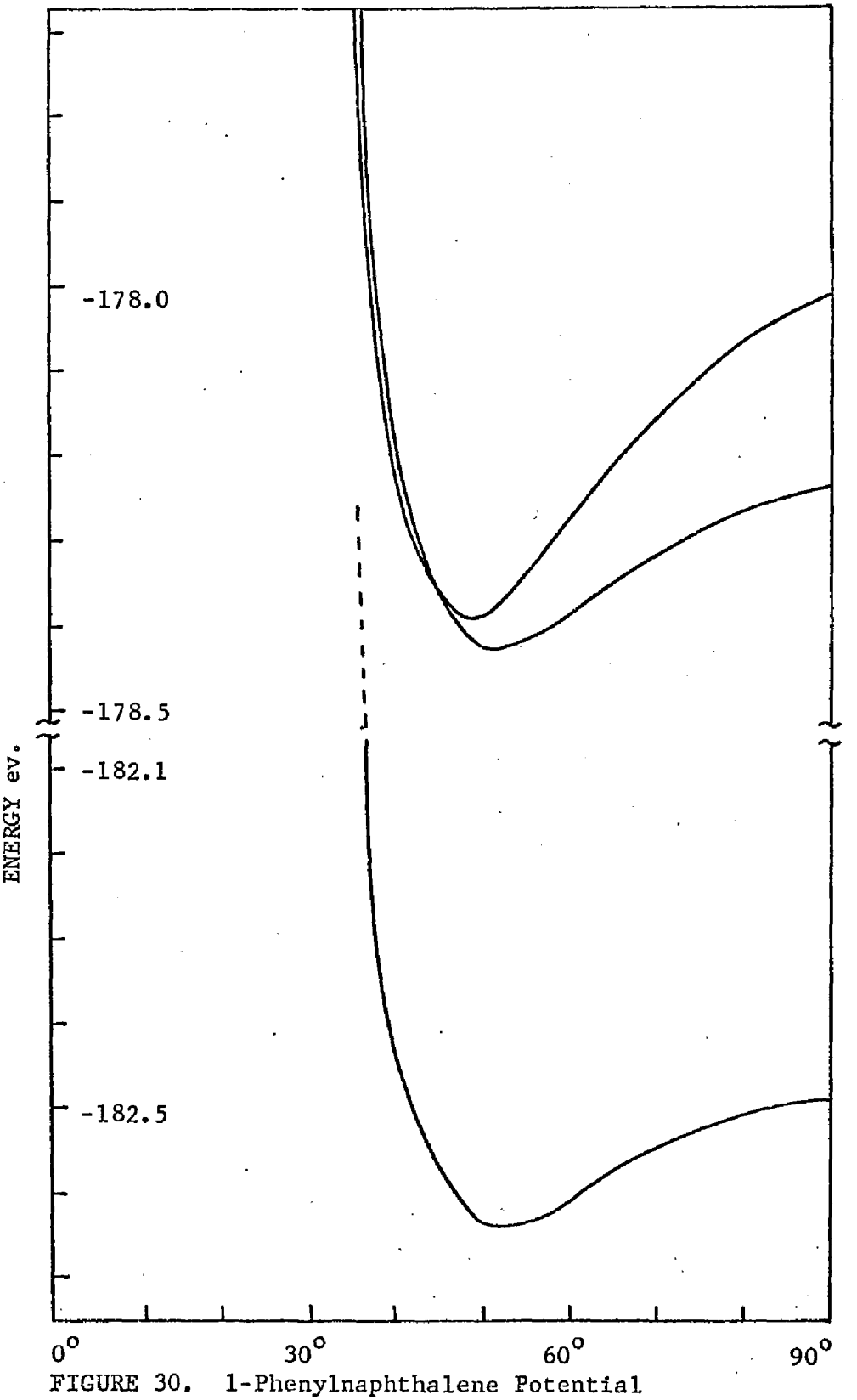

FIGURE 30. 1-Phenylnaphthalene Potential Energy Diagram

for the $^1L_{bN}$ state it is 0.197ev (4.54 kcal./mole), and for the $^1L_{aN}$ state it is 0.383ev (8.83 kcal./mole). The nature of the $^1L_{bN}$ and $^1L_{aN}$ potential curves near the molecular equilibrium position is an intriguing one. According to the prediction the equilibrium $^1L_{bN}$ state should be the lowest energy excited state. However, this equilibrium state is only 0.033ev (0.76 kcal./mole) lower in energy than the equilibrium $^1L_{aN}$ state and the energy difference for crossover between states is predicted to be only 0.063ev (1.45 kcal./mole).

Two experimentally interesting possibilities arise from this calculation. In 1-phenylnaphthalene the excited state potential wells are symmetrical about 90^o. If the phenyl ring were substituted in the twelve or the sixteen position, the potential well would no longer be symmetrical. See Figure 31a. If this substituent interacted strongly enough with the naphthalene ring, not only would the excited state potential wells be at different energetic positions on either side of 90^o, but the lowest energy excited state might be $^1L_{bN}$ when the substituent was interacting short axis with naphthalene and $^1L_{aN}$ when the substituent was interacting long axis with naphthalene. The requirements for the substituent would be that it be small, to keep θ as small as possible, and that it

be as electronegative as possible. Under these conditions, with the potential barrier at 90° greater than or on the order of 3½ kcal./mole it should be experimentally possible to observe to molecular fluorescences from the molecule. Probably the best compounds from which to observe this phenomena would be 2'-fluoro or 2'-chloro-1-phenylnaphthalene. It is probable that liquid helium temperatures would be required for the experimental work in order to obtain sufficient resolution to resolve the emissions. Evidence has been recently given substantiating hydrogen-halogen interactions in very similar compounds.[69]

Another possibility for observing two distinct molecular fluorescences in situations similar to this one exists. If the potential wells were shifted in the manner shown in Figure 31b and if there should exist a large enough energy difference for crossover between the two lowest lying excited state due to a significant geometrical difference between the two equilibrium excited states and if the energy difference were large enough so that a quantum could be trapped in either state there should be a distinct possibility to observe two

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[69] H.E. Holloway, loc. cit.

molecular fluorescences simultaneously. Somewhat similar, though externally produced, examples of this phenomena have been recently reported.[70,71] In reference 71 the excited states involved were triplet states and they were shifted with respect to each other by solvent interactions, but the principle involved is the one that must be employed with the 1-phenylnaphthalene excited singlet states. Contemplation of Figure 31 shows that what is required is to have a large energy difference for crossover between the $^1L_{bN}$ and the $^1L_{aN}$ states and to shift one or the other of these states or both so that they are not energetically degenerate with each other at the same ring angle at which their energetic minima occur. The best chance for observing this effect would likely be realized by using either fluorine or chlorine as substituents in either the 2-position or the 9-position on the naphthalene ring. (See Figure 28). Again, because of the low potential barrier between the excited states one would probably have to work at liquid helium temperature in order to observe the desired effect.

D. 1-Phenylnaphthalene, Comparison of Theory and Experiment

In order for calculations of this type to have

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[70] Noboru Mataga, and Yoshikazu Torihashi, and Kiyoshi Eyumi, Theoret. Chim. Acta, 2, (27) 158 (1964).

[71] N.C. Yang and Steven Murov, J. Chem. Phys., 45, 4358 (1966).

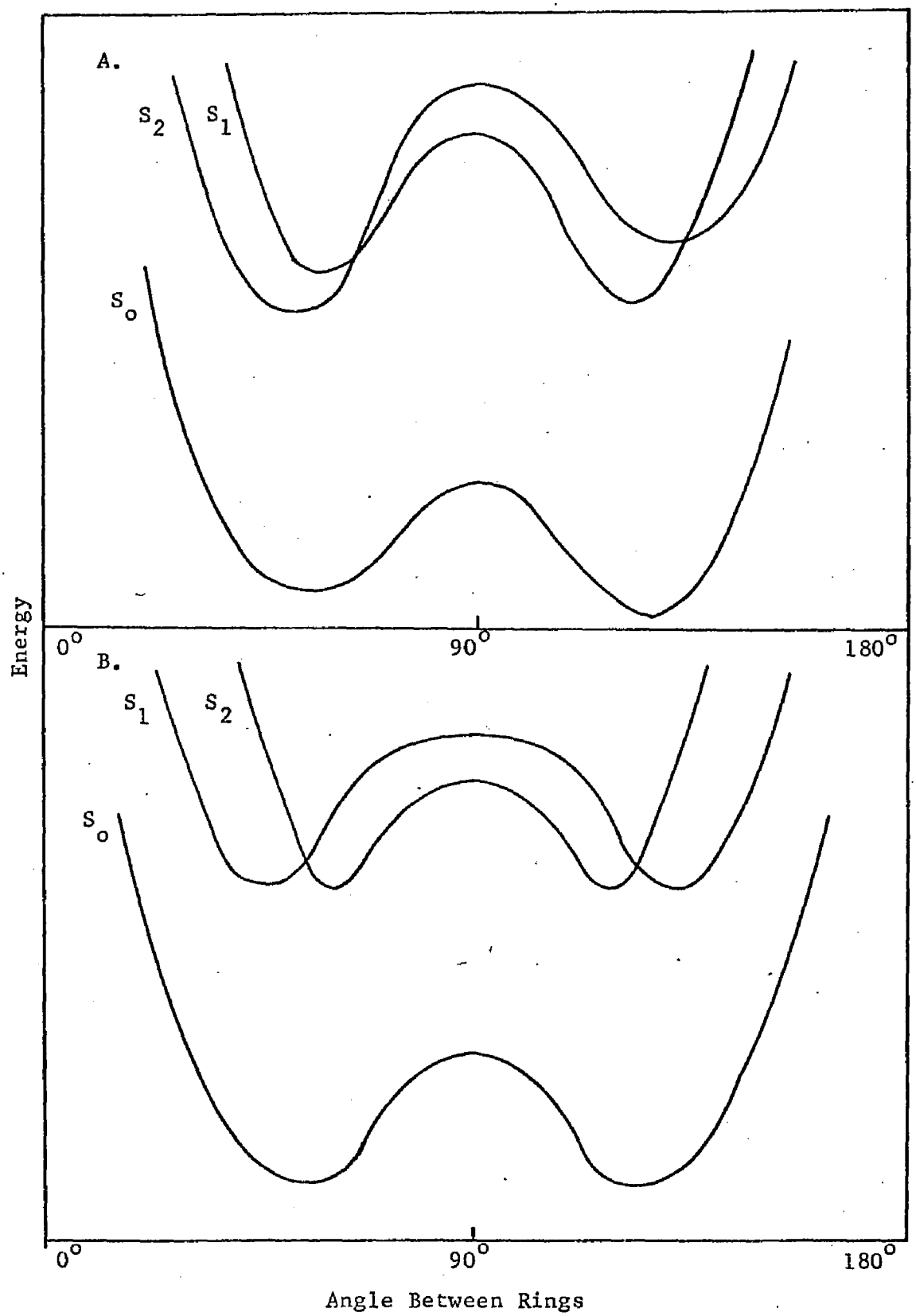

Figure 31. Some Proposed Potential Energy Diagrams

meaning the theoretical models must be applied to experimental molecules. There are two experimental models with which the 1-phenylnaphthalene calculation can be correlated. The first of these is, of course, the 1-phenylnaphthalene molecule, Figure 2. The other set of experimental models is 3,4-benzfluorene, Figure 8, and benzanthrene, Figure 12, in which the phenyl ring is fused to the naphthyl ring in the 1-position.

1-Phenylnaphthalene seems to fit the 55^{o} SCF-MO-CI model better than the 45^{o} model. In Table XXXII the experimental and theoretical values for singlet transition energies are compared. The first temptation is to try to make an experimental fitting for the $^{1}A \rightarrow {}^{1}M_{a}$ and the $^{1}A \rightarrow {}^{1}M_{b}$ transitions with the 1-phenylnaphthalene absorption spectrum. The absorption spectrum maintains a rather high extinction coefficient throughout the ultraviolet region, and is composed of broad bands. No definitive case can be made either for the experimental existence of these transitions or for their absence in the spectrum. However, the $^{1}A \rightarrow {}^{1}M_{a}$ and the $^{1}A \rightarrow {}^{1}M_{b}$ transitions could easily be postulated to lie on either side of the $^{1}A \rightarrow {}^{1}B_{bN}$ transition in spectra obtained from hydrocarbon solutions at ambient temperatures. What is more definitive is the correlation of temperature effects

TABLE XXXII

Comparison of Experimental and Theoretical
1-Phenylnaphthalene Transition Energies

Transition	Energy cm^{-1}		Theory	Exp.
	Theoretical	Experimental	Osc. Strength	ϵ
$^1L_{aN}$		35,340[a]		1.8×10^3
		34,660[b]		
	34,720		0.471	
$^1L_{bN}$		30,300[a]		
		31,330[b]		
		32,050[c]		
		31,000[d]		
	34,090		0.000	
^1M_a	43,470		0.228	
$^1B_{bN}$		46,730[a]		5.5×10^4
		44,640[c]		
	46,390		1.360	
^1M_b	47,143		0.428	
$^1B_{aN}$	53,150		0.451	

a = Vapor phase absorption spectrum. See Figure 2.
b = Absorption spectrum at 77°K in EPA. See Figure 3.
c = Room Temperature absorption spectrum in mixed hydrocarbon solvent. See Figure 2.
d = 0-0 band in 77°K fluorescence spectrum from hydrocarbon solvent. See Figure 4.

on experimental spectra with those predicted from the potential well diagrams. Because of the shallow nature of the ground state potential well significant populations of molecules distributed over a wide range of angles are expected at moderate temperatures. At room temperature kT is large enough so that significant molecular populations will occur at angles between 49^{o} and 56^{o} in the electronic ground state. See Figure 30. This is equivalent to saying that each observed electronic transition will originate from many slightly different molecules. These conclusions are consistent with the diffuse nature of the room temperature absorption spectra. As the temperature is lowered only molecular configurations nearer and nearer the position of equilibrium of the potential minimum are allowed. It is not suprising that at $77^{o}K$ the absorption spectrum shows considerable structure. The same arguments apply to the excited state potential well distributions, so the same trends are expected for transitions in the reverse direction. At $77^{o}K$ the fluorescence is so structured that it bears little resemblence to the fluorescence measured at room temperature which contains no fine vibrational structure. The fact that the minimum in the $^{1}L_{bN}$ potential well occurs at almost the same angle as that

of the ground state is consistent with the small shift between fluorescence and absorption 0-0 bands.

The fit between experiment and theory in the case of the triplet states is somewhat disappointing. If the 55^{o} molecular configuration is chosen to be the model for the triplet state, it is noted in Table XXXI that the $S_o \rightarrow T_1$ transition is predicted to occur at 16,900 cm^{-1} (5915Å). Experimentally the $S_o \leftarrow T_1$ phosphorescence is observed at about 20,450 cm^{-1} (4890Å). See Figure 4. This is a discrepancy of 3,550 cm^{-1}. Vibrationally the phosphorescence is typical of that occuring from an $^3L_{aN}$ state, which is in agreement with theory. The lack of fine structure in the phosphorescence is indicative of a very shallow potential well for the first excited triplet state. It appears that even at $77^{o}K$ significant populations of a broad range of angles is allowed in the $^3L_{aN}$ state.

E. Assignment of Transitions in 3,4-Benzfluorene and Benzanthrene

Comparison of the 0^{o} calculation can be made with experimental measurements made on 3,4-benzfluorene and benzanthrene. The electronic spectra of these compounds were characterized in the experimental section. Before comparisons can be made with

calculations it must be recalled that a significant but quantitatively undetermined interaction between ring systems takes place through the methylene bridge. The calculation completely ignores this interaction. The theoretical values have previously been tabulated in Table XXVIII and in Figure 29. The absorption spectra of 3,4-benzfluorene and benzanthrene are so finely structured and so rich in transitions that while the author has confidence that the assignments which are to be made on the basis of the theory are the most probable ones, but in some cases they are not the only ones possible.

3,4-Benzfluorene will be considered first. See Figure 8. The lowest energy transition at 29,735 cm^{-1} (3363Å) is the $^1A \rightarrow {}^1L_{aN}$ transition and lies at 2,600 cm^{-1} lower energy than that theoretically predicted. Detailed consideration of the low temperature absorption spectrum indicates that the $^1A \rightarrow {}^1L_{bN}$ transition probably occurs at about 32,200 cm^{-1} (3106Å). It is at this point that serious disturbance in the $^1A \rightarrow {}^1L_{aN}$ vibrational pattern begins. A weak transition begins at 37,260 cm^{-1} (2684Å). Three vibrational bands of this transition are discernible in the absorption spectrum and the $0 \rightarrow 1$ vibrational mode is favored. This transition is predicted to be totally

forbidden and from the SCF-MO calculation is assigned to the ψ_8^{12} transition. It is felt that its experimentally allowed character ($\epsilon \sim 6{,}000$) arises because of its proximity to two highly allowed transitions. Energetically the next transition exhibits a 0-0 band at 39,700 cm^{-1} (2519Å). This sharp band series is assigned to the $^1A \rightarrow {}^1M_a$ transition. The ^1M_a state is predicted to lie 41,400 cm^{-1} above the ground state. The $^1A \rightarrow {}^1B_{bN}$ and the $^1A \rightarrow {}^1M_b$ transitions remain to be assigned. The intense transition at 43,380 cm^{-1} (2305Å, ϵ = 46,700) is assigned to the $^1A \rightarrow {}^1B_{bN}$ transition while the transition at 46,730 cm^{-1} (2140Å) is assigned to the $^1A \rightarrow {}^1M_b$ transition. Experimentally the transition energies generally are to the red of the theoretical predictions. These shifts can be easily justified because of the increased interaction between rings through the methylene bridge.

The transition assignments are not as easily made in the case of benzanthrene. See Figure 12. The lowest energy transition at 28,610 cm^{-1} (3495Å), however, can easily be assigned to $^1A \rightarrow {}^1L_{aN}$. The relatively larger red shift is likely the result of increased naphthalene short-axis interaction. A group of low intensity bands occur between 33,760 (2960Å) and

35,100 cm^{-1} (2950Å). Part of these bands certainly belong to the $^1A \rightarrow {}^1L_{bN}$ progression and some contribution may still be made from the higher lying $^1L_{aN}$ vibrational states. The bands that were assigned to the ψ_B^{12} transition in 3,4-benzfluorene are not discernible. Three sharp bands are visible beginning at 38,910 cm^{-1} (2571Å). These bands are assigned to the $^1A \rightarrow {}^1M_a$ electronic transition. Since the $^1A \rightarrow {}^1B_{bN}$ transition is long axis polarized it is not suprising that the next highest transition is blue shifted over its counterpart in 3,4-benzfluorene; consequently, the transition at 41,900 cm^{-1} (2287Å) is assigned as the $^1A \rightarrow {}^1B_{bN}$ transition. Theoretically the $^1A \rightarrow {}^1M_b$ transition is also strongly long axis polarized. Assignment of the 45,045 cm^{-1} (2230Å) band to the $^1A \rightarrow {}^1M_b$ transition would require that the transition red shift with respect to its counterpart in 3,4-benzfluorene. Since this large red shift is inconsistent with the experimental evidence, the band at 45,045 cm^{-1} will be considered to be a member of the vibrational progression of the $^1A \rightarrow {}^1B_{bN}$ transition. These assignments force the conclusion that the $^1A \rightarrow {}^1M_b$ transition lies out of the experimentally accessible ultraviolet region.

The significant role that the methylene hydrogens play in the triplet state force the phosphorescences of these

compounds to much lower energies. See the experimental section. Comparison of the experimental phosphorescences with the theoretical predictions made for the triplet state, although gratifying, is very likely misleading. Therefore no attempt will be made to correlate the experimental and theoretical values.

F. Assignment of Transitions in 1,2-Benzfluorene, 2,3-Benzfluorene and the Dibenzfluorenes

The assignment of the transitions in 1,2- and 2,3-benzfluorene and the dibenzfluorenes would be tentative at best if based only on the calculation for planar 1-phenylnaphthalene. Fortunately further theoretical evidence is available.[72] A calculation has been made on 2-phenylnaphthalene that used parameters identical with those used for the planar 1-phenylnaphthalene calculation. In Table XXXIII the appropriate values for the singlet planar 2-phenylnaphthalene transitions are given. Briefly a few observations will be made. All experimentally interesting long-axis polarized transitions in 2-phenylnaphthalene have shifted considerably red of their counterparts in 1-phenylnaphthalene. The oscillator strengths for the allowed long-axis

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[72]The author wishes to express his thanks to Professor James Wharton who made available the theoretical data included in Table XXXIII.

TABLE XXXIII

2-Phenylnaphthalene, 0°, Singlet Transitions

Transitions		Energy						
		ev	cm^{-1}	Å	F	M	Trans. Pol. deg. from x	D.M.
ψ_8^9	$^1L_{aN}$	4.2886	34,592	2891	0.320	0.924	24	1.490
ψ_8^{10}	$^1L_{bN}$	4.0699	32,828	3046	-----	-----	36	9.14
ψ_8^{11}	?	4.6725	37,688	2653	-----	-----	148	14.58
ψ_8^{12}	?	5.6565	45,625	2192	-----	-----	136	2.61
ψ_8^{13}	F_N	5.8282	47,010	2127	-----	-----	115	2.79
ψ_7^9	$^1B_{bN}$	4.9340	39,798	2513	1.758	2.017	151	6.16
ψ_7^{10}	$^1B_{aN}$	5.7705	46,545	2148	0.185	0.605	145	0.60
ψ_7^{11}	?	6.2465	50,384	1985	-----	-----	14	3.34
ψ_7^{12}	?	6.2671	50,550	1978	-----	-----	2	0.10
ψ_6^9	^1M_a	5.9707	48,160	2076	0.372	0.844	55	1.54
ψ_5^9	^1M_b	6.0581	48,865	2046	0.750	1.890	6	3.10
ψ_5^{10}	?	6.5924	53,174	1881	0.017	0.170	178	1.88
ψ_4^9	$^1C_{bN}$	6.2881	50,720	1972	0.110	0.447	66	2.06

polarized transitions are significantly higher than their counterparts in 1-phenylnaphthalene. The $^1A \rightarrow {}^1L_{aN}$, the ψ_8^{12} and the $^1A \rightarrow {}^1M_a$ transitions have shifted to the blue of their counterparts in 1-phenylnaphthalene although the $^1A \rightarrow {}^1M_a$ and the $^1A \rightarrow {}^1L_{aN}$ transitions have retained their allowed character.

With these observations in mind the transitions in 2,3-benzfluorene will be assigned. See Figure 15. The lead transition which begins at 29,438 cm^{-1} (3397Å) is assigned to the $^1A \rightarrow {}^1L_{bN}$ transition. Several vibrational bands belonging to this transition are visible and it has a suprisingly high extinction coefficient, 7000 l./m.cm. The magnitude of the extinction of this transition must be attributed to significant long-axis interaction of the naphthalene submolecule through both a fusing bond and a bridging bond with the phenyl ring. The onset of the $^1A \rightarrow {}^1L_{aN}$ transition is at 31,397 cm^{-1} (3185Å). In the ambient temperature absorption spectrum at least three members of the vibrational progression are visible. At 77°K, many bands are resolved in this region and it is thought that the vibrational progressions of both the $^1A \rightarrow {}^1L_{aN}$ and the $^1A \rightarrow {}^1L_{bN}$ transitions are superimposed. The $^1A \rightarrow {}^1B_{bN}$ transition

begins at 37,665 cm^{-1} (2655Å). Unlike its counterpart in 3,4-benzfluorene the $^1A \rightarrow {}^1B_{bN}$ transition in 2,3-benzfluorene is well resolved and very intense. The extinction coefficient of this transition in 2,3-benzfluorene is 69,500 l./m.cm. in comparison with 46,700 l./m.cm. in 3,4-benzfluorene. The transition also is at about 3,540 cm^{-1} lower energy than its counterpart in 3,4-benzfluorene. The remaining transition centered at 46,425 cm^{-1} (2154Å) is assigned to the $^1A \rightarrow {}^1B_{aN}$ transition. It is interesting to note that in the 2-phenylnaphthalene calculation this transition is predicted to occur at lower energy than the $^1A \rightarrow {}^1C_{bN}$ transition. It is also interesting that the entire ultraviolet spectrum of 2,3-benzfluorene has been assigned without invoking any whole molecule transitions. These transitions theoretically occur at higher energy in 2-phenylnaphthalene than in 1-phenylnaphthalene. It is likely, however, that the $^1A \rightarrow {}^1M_a$ and the $^1A \rightarrow {}^1M_b$ transitions (both allowed) contribute to the extinction of the broad band that was assigned as the $^1A \rightarrow {}^1B_{aN}$.

The spectrum of 1,2-benzfluorene is only slightly different from that of 2,3-benzfluorene. See Figure 17. The lead transition beginning at 29,112 cm^{-1} (3435Å) is assigned

to be $^1A \rightarrow {}^1L_{bN}$. The decrease in extinction coefficient to 1,100 l./m.cm. from 7,000 l./m.cm. for that of 2,3-benzfluorene is a result of the loss of the long-axis bridging bond on the naphthalene submolecule. The 0-0 band of the $^1A \rightarrow {}^1L_{aN}$ transition occurs at 31,397 cm^{-1} (3185Å). Because of the lower intensity of the $^1A \rightarrow {}^1L_{bN}$ transition the 77°K absorption of the $^1A \rightarrow {}^1L_{aN}$ transition is uncluttered by the $^1A \rightarrow {}^1L_{bN}$ vibrational peaks. The $^1A \rightarrow {}^1B_{bN}$ transition begins at 37,951 cm^{-1} (2635Å) which is only a slightly higher energy than its counterpart in 2,3-benzfluorene. The $^1A \rightarrow {}^1B_{aN}$ transition is missing from the spectrum of 2,3-benzfluorene. The absence of this transition is attributed to the loss of the long-axis interaction because the bridging bond was moved from the 2-naphthyl position.

An attempt will also be made to assign the transitions in 1,2,7,8-dibenzfluorene and 3,4,5,6-dibenzfluorene spectra. Submolecule transitions should retain their identity in much the same manner as that observed in the case of the benzfluorenes. It is the molecular transitions which are expected to exhibit the greatest deviation from those predicted for the phenylnaphthalenes. It is likely that the molecular transitions will occur to the red of the predicted values and that they will have higher intensities than their counterparts in the benzfluorenes. Also

it is relevant to note that there will be two naphthalene submolecule transitions for every one that occurred in the benzfluorenes. There is reason to expect, particularly in the case of 1,2,7,8-dibenzfluorene, that exciton interaction will occur between halves of the molecule. Although there were observed experimentally some small splittings in transitions which may be due to this effect no extended discussion will be devoted to the phenomenon. The 3,4,5,6-dibenzfluorene molecule will be considered first.

In 3,4,5,6-dibenzfluorene the lowest energy transition is the $^1A \rightarrow {}^1L_{aN}$ which begins at 27,360 cm^{-1} (3655Å). See Figure 6. A very weak transition occurs at 36,050 cm^{-1} (2774Å). This transition is assigned to a whole molecule transition. Its counterpart in 1-phenylnaphthalene is the forbidden ψ_8^{12} transition. Its intensity is attributed to intensity borrowing from the highly allowed transitions very near it. The transition with a 0-0 band at 38,212 cm^{-1} (2617Å) which exhibits three sharp vibrational peaks is assigned to the $^1A \rightarrow {}^1M_a$ molecular transition. The $^1A \rightarrow {}^1B_{bN}$ transition is relatively weaker than might be a priori expected and is located at 40,700 cm^{-1} (2457Å). Its intensity is in line with predictions

made in the 1-phenylnaphthalene calculations. The $^1A \rightarrow {}^1B_{bN}$ and the $^1A \rightarrow {}^1L_{aN}$ transitions are predicted to have comparable transition moments. The transition at 46,470 cm^{-1} (2152Å) is assigned to the $^1A \rightarrow {}^1M_b$ transition. Theoretically this transition is predicted to occur at 46,430 cm^{-1} and is predicted to have a transition moment about 1.5 times that of the $^1A \rightarrow {}^1B_{bN}$ transition.

The lowest energy transition in 1,2,7,8-dibenzfluorene is at 27,940 cm^{-1} (3579Å) and is assigned as the $^1A \rightarrow {}^1L_{bN}$ transition. See Figure 21. The 0-0 band of the $^1A \rightarrow {}^1L_{aN}$ transition is at 28,893 cm^{-1} (3461Å). This band seen in the low temperature spectrum is observed as a shoulder at 3457Å in the ambient temperature spectrum. The vibrational progression in the $^1A \rightarrow {}^1L_{aN}$ transition is not nearly as well defined as it is in the 1,2-benzfluorene spectrum. See Figure 17. In addition the Franck-Condon contour of the $^1A \rightarrow {}^1L_{aN}$ transition bears little resemblence to its counterpart in 1,2-benzfluorene. The 0-0 band of the $^1A \rightarrow {}^1B_{bN}$ transition is at 36,982 cm^{-1} (2704Å) and the transition exhibits four vibrational maximal. Its high intensity is a result of the fusing in the 2-naphthyl positions. Theoretically (from the

1-phenylnaphthalene calculation) its transition moment is over twice that of the $^1A \rightarrow {}^1L_{aN}$ transition. A transition exists at slightly lower energy than the $^1A \rightarrow {}^1B_{bN}$. Its 0-0 band is at 34,530 cm^{-1} (2896Å), and the transition exhibits four vibrational maxima. Since no transition was predicted in this region in the 2-phenylnaphthalene calculation it must arise because of interaction through the methylene bridge which joins the naphthalene short-axis positions. This transition is assigned to the molecular $^1A \rightarrow {}^1M_a$ transition although it is a little suprising that it exhibits such a high intensity in this molecule. One additional transition is visible in the ambient temperature absorption spectrum. It occurs at 46,922 cm^{-1} (2128Å). Because of its intensity and its energetic position, the most logical assignment (from either the 1-phenylnaphthalene or 2-phenylnaphthalene calculations) is that this is the molecular $^1A \rightarrow {}^1M_b$ transition.

A summary of the SCF-MO-CI calculation at angles other than 90°, the hydrogen repulsion calculation, the comparison between theoretical and experimental models and the assignment of experimental transitions follows:

1. In the 1-phenylnaphthalene calculation as the phenyl ring was rotated from 90°, occupied and unoccupied MO's

were observed to delocalize over both rings;

2. The extent of delocalization was defined and calculated for each important MO;

3.. In view of this calculation the theoretical transitions were characterized and were followed as a function of ring angle. It was found that typically benzene transitions were no longer experimentally important while many naphthalene transitions retained their identities. A new set of whole molecule transitions was predicted;

4. The SCF-MO-CI calculation for triplet states was considered and was found to be in poorer agreement with experiment than the singlet calculation;

5. The failure of the SCF-MO-CI calculation to recognize hydrogen-hydrogen interaction contributions to molecular energies was recognized and new sets of ground and excited state potential wells as a function of molecular geometry were generated;

6. In view of these calculations, the molecular states were considered to be a function of geometry and previously unobserved phenomena were predicted to exist for, as yet, unsynthesized molecules;

8. Comparisons were made of the 0^{o} SCF-MO-CI, 1-phenylnaphthalene calculation with benzanthrene and with 3,4-benzfluorene. The theoretical calculations made possible the assignment of all transitions experimentally observed in these compounds;

9. By using a 0^{o} SCF-MO-CI calculation done by another author on the 2-phenylnaphthalene molecule in conjunction with the 1-phenylnaphthalene calculation, assignments of all experimentally observed transitions in 2,3-benzfluorene, 1,2-benzfluorene, 1,2,7,8-dibenzfluorene and 2,3,4,5-dibenzfluorene were made.

G. The 2,3-Benzbiphenylene Calculation

A SCF-MO-CI calculation was also carried out on 2,3-benzbiphenylene. The benzbiphenylene molecule is depicted in Figure 32.

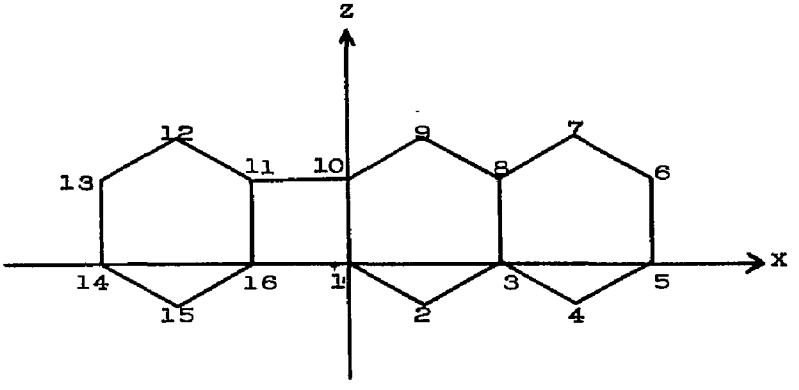

FIGURE 32. The 2,3-Benzbiphenylene Molecule

All bond lengths in the six-membered rings were taken to be 1.40Å. Bonds 10-11 and 1-16 were assumed to be 1.50Å in length. Except for β_{10-11} and β_{1-16}, values identical to those used in the case of 1-phenylnaphthalene were employed. The values for β_{10-11} and β_{1-16} were a source of some concern. These values should be indicative of the type of bonding between the 10-11 and the 1-16 carbons. At one extreme (less negative β) the system can be considered to be a naphthalene interacting through two fusing single bonds with a benzene, much as in the 0^{o}, 1-phenylnaphthalene calculation. At the other extreme (more negative β) the molecule can be considered to be fully alternate and fully aromatic. In the first case it is reasonable to expect the lowest energy transition to be $^{1}A \rightarrow {}^{1}L_{b}$ in character and rather severely red shifted with respect to that of naphthalene because all interaction with naphthalene is in the long axis direction. On the other hand, if the molecule is fully aromatic the lowest energy transition should be $^{1}A \rightarrow {}^{1}L_{a}$, and the absorption spectrum should be reminiscent of anthracene. Further, if the molecule is fully aromatic the four-membered ring would be essentially a cyclobutadiene ring. This ring system is so unstable, however, that chemists have been trying

for twenty-five years to prepare it. The experimental absorption spectrum does not clarify the situation. Experimentally the first transition is not typically $^1A \rightarrow {}^1L_b$ in character and the whole ultraviolet spectrum is not characteristic of an anthracene molecule. Furthermore, the molecule is stable in air in the liquid state ($T \sim 500^{\circ}K$) and does not visibly decompose photochemically.

Molecules containing four-membered rings fusing other ring systems together have been theoretically considered previously.[73,74,75,76,77] None of these calculations were as sophisticated as the modified P.P.P. calculation and none were applied to 2,3-benzbiphenylene. The conclusions of these calculations did not serve to characterize the properties of benzbiphenylene.

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A value for $\beta_{10-11} = \beta_{1-16} = -2.10$ was chosen. The electronic transitions predicted for benzbiphenylene were much the same as the experimentally observed ones but were predicted to occur significantly to the blue of their experimental counterparts. The Coulson[78] relationship shown in equation 24

$$P_{rs} = \tfrac{1}{2}\, \partial E/\partial \beta_{rs} \qquad \ldots\ldots 24$$

was used to determine the value of β necessary to give an experimental fit with what was felt to be the $^1A \rightarrow {}^1B_b$ transition. The necessary value for β was -2.39. It is certainly worthy of note that this is exactly the same value that β takes between adjacent carbon atoms in the benzene and naphthalene rings. This value may be slightly too negative. It is reasonable to expect that if the interaction between the rings is as large as predicted by the β value, that the bond length between rings will be less than 1.50Å. Small changes in bond lengths have only a very small effect on the transition energies predicted by the CI calculation. Therefore changing the fusing bond lengths and adjusting β to obtain an experimental fit would have only a very small effect on the final value for β. The net effect on β would be to make it slightly less negative.

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In Table XXXVI the predicted values for bond orders in the ground state and three important excited states are given. The 1-16 and 10-11 bond orders in the ground state have low values. These values may have been artificially lowered because of the long bond distances programmed into the calculation. It is worth noting that these bond orders are significantly higher in the excited states considered in Table XXXV. The 1-10 and 11-16 bond orders are also lower than those that would be expected for mono-substituted naphthalenes and benzenes. This could be interpreted to be an attempt to distribute electronic charge about the four-membered ring. Notably the 1-10 bond order is lower than that of the 3-8 bond, which is normally low for naphthalene.

In Table XXXV the theoretical values are given for transition energies, oscillator strengths, transition moments, transition polarizations and dipole moments for the lowest energy singlet transitions. With the exception of one forbidden transition, ψ_8^{13}, the transition polarizations are very pure either short-axis or long-axis. The dipole moments in the excited states for all allowed transitions are low enough to be consistent with present theories. The lowest energy transition, $^1B_1 \rightarrow {}^1A_2$, is an $^1A \rightarrow {}^1L_a$ type transition and is predicted to occur at

TABLE XXXIV

2,3-Benzbiphenylene Bond Orders

Bond	States			
	S_o	^1L_a	^1L_b	^1B_b
1-2	.764	.640	.611	.607
1-10	.489	.260	.437	.434
1-16	.239	.490	.363	.369
2-3	.496	.588	.537	.542
3-4	.562	.527	.544	.544
3-8	.552	.423	.468	.487
4-5	.734	.748	.645	.646
5-6	.604	.531	.615	.621
6-7	.734	.748	.645	.646
7-8	.562	.527	.544	.544
8-9	.496	.588	.537	.542
9-10	.764	.640	.611	.607
10-11	.239	.491	.363	.369
11-12	.668	.580	.622	.621
11-16	.582	.305	.450	.445
12-13	.636	.711	.638	.641
13-14	.685	.513	.616	.616
14-15	.636	.711	.638	.641
15-16	.678	.581	.622	.621

TABLE XXXV

2,3-Benzbiphenylene Singlet Transitions

Transition			Energy						
Platt	SCF-MO	Group	ev	cm^{-1}	Å	F	M	Trans. Pol	D.M.
$^1A \rightarrow {}^1L_a$	ψ_8^9	$^1B_1 \rightarrow {}^1A_2$	3.3258	26,826	3728	0.010	0.181	z	1.865
$^1A \rightarrow {}^1L_b$	ψ_8^{10}	$^1B_1 \rightarrow {}^1B_1$	3.4615	27,920	3582	-----	-----	x	0.941
	ψ_8^{11}	$^1B_1 \rightarrow {}^1B_1$	4.4049	35,530	2814	-----	-----	x	5.593
	ψ_8^{12}	$^1B_1 \rightarrow {}^1A_2$	6.1972	49,987	2001	0.586	1.039	z	7.409
	ψ_8^{13}	$^1B_1 \rightarrow {}^1B_1$	5.3944	43,511	2298	-----	-----	mixed	5.720
$^1A \rightarrow {}^1B_b$	ψ_7^9	$^1A_2 \rightarrow {}^1A_2$	4.6013	37,114	2694	2.920	2.692	x	1.686
$^1A \rightarrow {}^1B_a$	ψ_7^{10}	$^1A_2 \rightarrow {}^1B_1$	4.4926	36,237	2760	0.116	0.544	z	3.129
	ψ_7^{11}	$^1A_2 \rightarrow {}^1B_1$	5.7202	46,139	2167	0.002	0.065	z	5.294
	ψ_7^{12}	$^1A_2 \rightarrow {}^1A_2$	5.9755	48,198	2075	-----	-----	x	2.884
	ψ_7^{13}	$^1A_2 \rightarrow {}^1B_1$	6.5268	52,645	1900	0.524	0.958	z	0.713
$^1A \rightarrow {}^1C_b$	ψ_6^9	$^1A_2 \rightarrow {}^1A_2$	5.9929	48,339	2067	0.190	0.603	x	3.169
	ψ_6^{10}	$^1A_2 \rightarrow {}^1B_1$	5.7547	46,417	2154	-----	-----	z	7.386
	ψ_5^9	$^1B_1 \rightarrow {}^1A_2$	6.0321	48,655	2055	-----	-----	z	0.334
	ψ_4^{10}	$^1A_2 \rightarrow {}^1B_1$	6.3177	50,958	1962	-----	-----	z	8.095

26,830 cm^{-1}. The forbidden long-axis polarized $^1A \rightarrow {}^1L_b$ transition, $^1B_1 \rightarrow {}^1B_1$ is predicted to occur at 27,920 cm^{-1}. Another long-axis polarized forbidden transition is predicted to occur at 35,530 cm^{-1}. An allowed transition $^1A \rightarrow {}^1B_a$, ψ_7^{10}, ($^1A_2 \rightarrow {}^1B_1$) which is short-axis polarized is predicted at 36,240 cm^{-1}. The $^1A \rightarrow {}^1B_b$ transition ($^1A_2 \rightarrow {}^1A_2$) which was fit with experiment is predicted to occur at 37,115 cm^{-1}. Three other experimentally interesting allowed transitions are predicted; the ψ_7^{11}, ($^1A_2 \rightarrow {}^1B_1$) which is slightly allowed is predicted at 46,140 cm^{-1}, the ψ_6^9 ($^1A_2 \rightarrow {}^1A_2$) which is more strongly allowed is predicted at 48,340 cm^{-1} and the ψ_8^{12} ($^1B_1 \rightarrow {}^1A_2$) which is strongly allowed at 50,000 cm^{-1}.

The agreement of theoretical predictions with experimental measurements although generally satisfactory, is not nearly as good as might be desired. The lowest energy transition, although the $^1A \rightarrow {}^1B_b$ energy was fit into the calculation, remains 990 cm^{-1} to the blue of the experimental value. From the extinction coefficient of this transition and from its general band contour there is little doubt that the lowest energy transition is the $^1A \rightarrow {}^1L_a$. It is unfortunate that a good absorption spectrum could not be obtained at 77°K. From

the amount of resolution at room temperature it is likely that the disturbing influence of the $^1A \rightarrow {}^1L_b$ transition could be observed in this spectrum. Experimental assignment of the onset of the $^1A \rightarrow {}^1L_b$ transition remains impossible. The fluorescence polarization curve, shown in the experimental section as Figure 23 indicates that the polarization remains positive and rather flat in the entire region from 3250-3900Å. This is easily justifiable because the extinction of the $^1A \rightarrow {}^1L_b$ relative to the $^1A \rightarrow {}^1L_a$ is on the order of 1:50 and the long axis influence due to the $^1A \rightarrow {}^1L_b$ transition would be very slight. Beginning at about 3250Å (30,770 cm^{-1}) the polarization curve dips sharply and becomes negative from about 3050-3170Å. There are two possible explanations for this observation. Underlying both, of course, is the fact that there must be a transition which is long-axis polarized which is most strongly absorbing in this region. One explanation would be that the extinction of the $^1A \rightarrow {}^1L_b$ transition has become stronger than the weakening vibrational progressions of the $^1A \rightarrow {}^1L_a$ transition and that this transition predominates in the spectrum. Some credence is lent to this theory because this is the general region in which one would expect a naphthalene-type $^1A \rightarrow {}^1L_b$ transition. However, it will

be recalled that the $^1A \rightarrow {}^1L_b$ transition was predicted to begin at 3580Å and this region is rather far removed from the region of negative polarization. The short-axis polarized $^1A \rightarrow {}^1B_a$, ψ_7^{10}, transition must be fit to the experimentally observed transition which begins at 2971Å (33,660 cm^{-1}). If the ψ_8^{11} transition is shifted red the same amount as it was necessary to shift the ψ_7^{10} transition to fit experiment, then the long axis polarized ψ_8^{11} transition is in the exact region which gives rise to the negative polarization. The abrupt change in the polarization curve suggests the onset of an oppositely polarized transition rather than the gradual change from dominance by one transition over another as was required in the previous explanation. It remains a mystery why the ψ_7^{10} and ψ_8^{11} transitions were predicted to be so blue of their experimental counterparts when the rest of the transitions were in much better agreement. The $^1A \rightarrow {}^1B_b$ transition was forced to fit the experiments. The only clarification which must be made is that of the polarization spectrum. The experimental points at wavelengths shorter than 2800Å are much less reliable than those at longer wavelengths. The slits on the exciting monochromator were much larger, the polaroid sheet used absorbs strongly in this region and the

emission light intensity from the sample is much smaller. If the present interpretations are taken to be correct the polarization curve at 2650 and 2700Å must not only be incorrect qualitatively but must also be incorrect in sign. These conclusions are not impossible to accept because in addition to the above mentioned factors it is a known characteristic of this monochromator that at short wavelengths with wide slits a considerable amount of scattered light of longer wavelengths is passed. Theoretically three further transitions of considerable intensity are predicted. All of these lie in the 2000-2200Å region and probably contribute to the observed absorption in this region which has a maximum at about 2070Å (48,310 cm^{-1}). In Table XXXVI a comparison is made between the theoretical and experimental transition energies.

The first three triplet states for 2,3-benzbiphenylene are predicted to be the ^3L_a, ^3L_b and ^3B_b in order of ascending energy. The $^1A \rightarrow {}^3L_a$ transition is predicted at 6752Å or 14,810 cm^{-1}. Even allowing for poor agreement between experiment and theory no emission was found in this general region. It is thought that the emission depicted in Figure 25 and discussed in the experimental section which arises from a dissociative state

TABLE XXXVI

Comparison of Experimental and Theoretical
2,3-Benzbiphenylene Transition Energies

Transition			Energy cm^{-1}	
Platt	SCF-MO	Group Theory	Theoretical	Experimental
$^1A \rightarrow {}^1L_a$	ψ_8^9	$^1B_1 \rightarrow {}^1A_2$	26,830	25,840[a]
$^1A \rightarrow {}^1L_b$	ψ_8^{10}	$^1B_1 \rightarrow {}^1B_1$	27,920	?
$^1A \rightarrow$?	ψ_8^{11}	$^1B_1 \rightarrow {}^1B_1$	35,530	31,550[b]
$^1A \rightarrow {}^1B_a$	ψ_7^{10}	$^1A_2 \rightarrow {}^1B_1$	36,240	33,660[a]
$^1A \rightarrow {}^1B_b$	ψ_7^9	$^1A_2 \rightarrow {}^1A_2$	37,114	37,010[a]
	ψ_6^9	$^1A_2 \rightarrow {}^1A_2$	48,339	48,310[c]
	ψ_8^{12}	$^1B_1 \rightarrow {}^1A_2$	50,000	?
	ψ_7^{11}	$^1A_2 \rightarrow {}^1B_1$	46,139	?

a - taken from absorption spectrum at 77°K in 3-MP solution

b - postulated from fluorescence polarization spectrum

c - Taken from absorption spectrum at room temperature in 3-MP solution

empties the triplet state so efficiently that essentially no molecular phosphorescence occurs.

A summary of observations made on the 2,3-benzbiphenylene molecule follows:

1. A very structured fluorescence was measured which showed the expected symmetry relationship with the absorption spectrum;

2. The absorption spectra of 2,3-benzbiphenylene indicated that the lowest energy transition is not typical of a long-axis substituted naphthalene molecule;

3. A delayed emission was measured in the same region as the fluorescence. This emission was attributed to a photochemical decomposition product which had to be produced reversibly;

4. MO calculations were made.

   (a) In order to obtain an experimental fit, β values between six-membered rings had to take the same value as those within the rings.

   (b) Electronic distributions and bond orders indicate that all electronic transitions were typical of whole molecule transitions.

   (c) Theoretically 2,3-benzbiphenylene is a fully

alternate, fully aromatic molecule containing a four-membered ring which is essentially a cyclobutadiene ring.

The PPP type calculation as performed on 2,3-benzbiphenylene gave results which were in poorer agreement with experiment than that usually expected for calculations on alternate hydrocarbons but were in significantly better agreement than the best calculations done to date on nonalternate hydrocarbons such as azulene. The calculation was sufficiently good so that the lowest energy transition could be unambiguously assigned and several higher energy transitions could be tentatively assigned.

The fit obtained between experiment and theory for 2,3-benzbiphenylene indicates to the author that theoretically the whole-molecule aromatic character has been slightly overestimated in the calculation. However, even allowing for this overestimation, one must conclude that aromatic character extends, to a large extent, over the whole molecule. No longer can the bonds between the phenyl and naphthyl rings be considered to be carbon-carbon single bonds. Theoretically and experimentally 2,3-benzbiphenylene cannot be classified as a composite molecule as defined early in this work.

V

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APPENDIX A

Glossary of Abbreviations

1. Å - Angstrom
2. ev - Electron Volt
3. IP - Isopentane hydrocarbon solvent
4. 3-MP - 3-Methylpentane hydrocarbon solvent
5. IPMP - Mixed hydrocarbon solvent, 3-MP and IP in a 1:6 volume ratio
6. mu - Millimicron
7. SCFMO - Self consistent field molecular orbital
8. CI - Configuration interaction

APPENDIX B

Spectra of the Anions of 1,2-Benzfluorene, 2,3-Benzfluorene, 3,4-Benzfluorene and Benzanthrene.

Taken From:

Streitwieser, A., Jr., and Brauman, J.I., J. Am. Chem. Soc., 85, 2633 (1963).

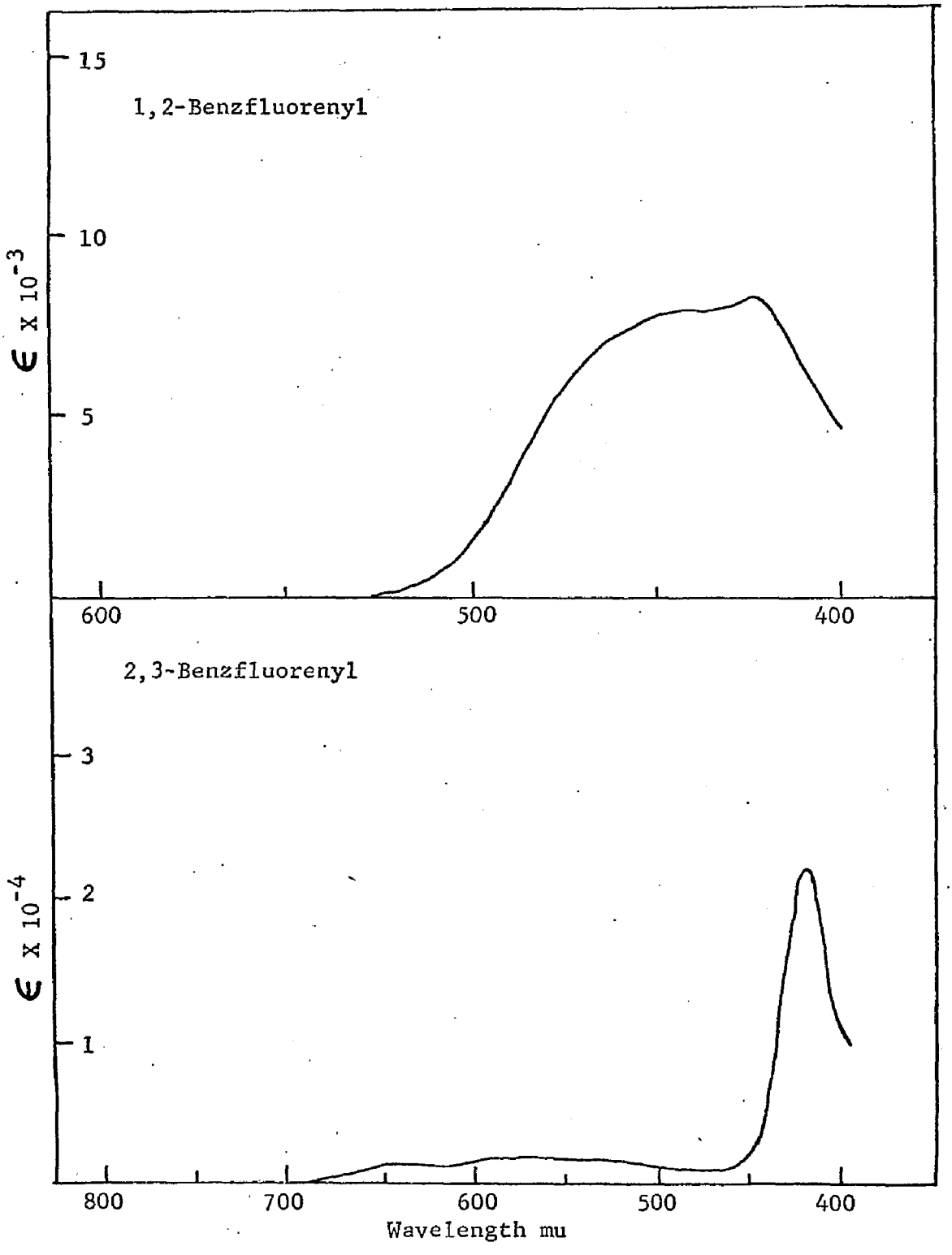

FIGURE 34. Visible Spectra of the Li Salts of 1,2-Benzfluorenyl and 2,3-Benzfluorenyl in Cyclohexylamine Solutions

VII

VITA

Jimmie Reed McDonald was born August 20, 1942 in Austin, Texas. He attended grade school in Jonah, Texas and graduated from Georgetown High School in Georgetown, Texas in 1960. He attended Southwestern University in Georgetown, Texas from 1960 to 1964 from which he received his Bachelor of Science degree in 1964. In 1964 he entered the Graduate School of the Louisiana State University in Baton Rouge, Louisiana where he is now a candidate for the degree of Doctor of Philosophy.

He married Lynette Cornitius in 1963 and has two children, Anna Marie and Jimmie Reed, Jr. born in 1967.

EXAMINATION AND THESIS REPORT

Candidate: Jimmie R. McDonald

Major Field: Chemistry

Title of Thesis: A Study of the Electronic States of 1-Phenylnaphthalene Bridged Phenylnaphthalene and Binaphthyl Derivatives

Approved:

Robert V. Kaufman
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Sp. Mc Glynn

William T. Burnett, Jr.

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James H. Thaxton

Date of Examination:

May 3, 1968